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ANALYTICAL REFERENCE SERVICE TRAINING PROGRAM. WATER MINERALS NUMBER 3

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

November 1961

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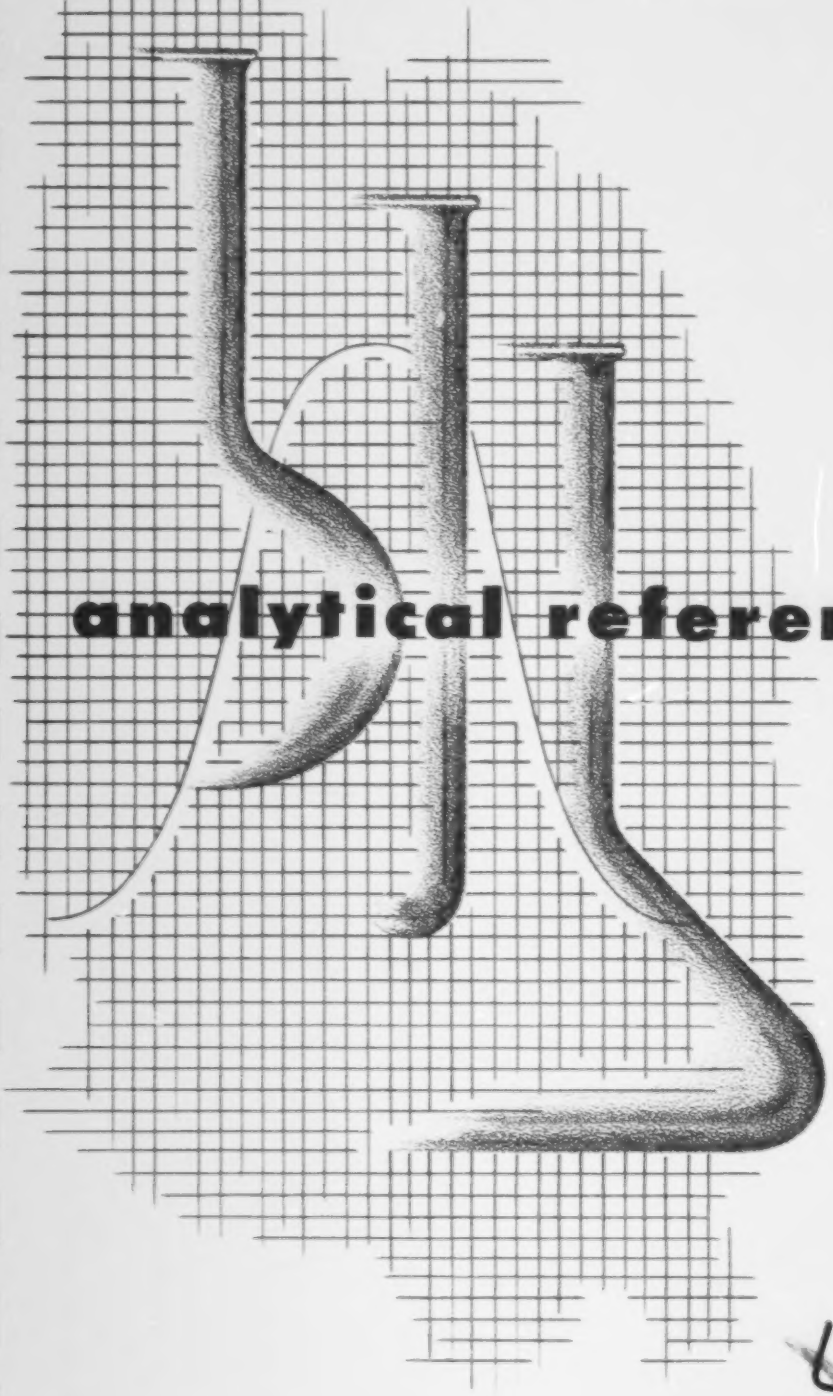

WATER MINERALS
NUMBER 3
NOVEMBER, 1961

analytical reference service

TRAINING PROGRAM

Robert A. Taft

SANITARY ENGINEERING CENTER

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
CINCINNATI, OHIO

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ANALYTICAL REFERENCE SERVICE

WATER-MINERALS No. 3

Report of a laboratory performance study conducted jointly with the participating member organizations.

Prepared by the

Analytical Reference Service

TRAINING PROGRAM

U.S. DEPARTMENT OF HEALTH, EDUCATION AND WELFARE
Public Health Service
Bureau of State Services
Division of Engineering Services

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

1961

ANALYTICAL REFERENCE SERVICE

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FOREWORD

The Analytical Reference Service is conducted by the Robert A. Taft Sanitary Engineering Center to provide a means of evaluating laboratory methods in the field of environmental sciences and engineering. Membership includes Federal, state, and municipal agencies, industries, universities, consulting firms, and foreign agencies. Cooperative studies by member organizations, through analysis of identical samples of environmental media and critical review of methodology, provide the mechanism for:

1. Statistical evaluation of procedures, including precision and accuracy.

2. Comparison of analytical procedures and results between laboratories having similar responsibilities.

3. Exchange of information regarding weaknesses of currently approved methods.

4. Further development of methods or entirely new approaches.

5. Broad-scale evaluation of new analytical methods.

Initially directed toward examination of water, the studies have been broadened to include other media. Samples are designed and prepared to contain measured amounts of selected constituents. Decisions as to qualitative makeup are made by the staff of ARS, the membership, and consultants. Notice of a study is forwarded to each member with information regarding the qualitative makeup of the sample and special details regarding its handling.

Foreword

Following indication of a member's desire to participate in the study, a portion of the sample is shipped with accompanying data forms which provide space for numerical analytical values and a narrative critique of the procedures used. The laboratories are urged to comment on the methods, difficulties, modifications, sources of error, and other factors. Results are requested within sixty days.

The results and comments of each study are compiled, as in the accompanying report. Experience indicates that a repeat study produces a sizeable increase in the number of participants. In the 1956 water-minerals study, 19 agencies participated; in the 1958 study, 31 member agencies participated; 59 agencies have cooperated in this study.

A water-metals study has recently been completed, and the final report is being prepared. A water-trace elements sample, containing beryllium, boron, arsenic, and selenium was shipped to members in October. A milk sample is planned for the determination of DDT by a specified method. Studies for the determination of strontium-90 in water and SO_2 in air are in the planning stage.

Selection of these studies was guided by answers to the questionnaires distributed to member agencies to poll their interests. Results of this poll will continue to serve as a basis for planning future studies.

Membership now consists of 120 agencies of many diversified interests. The steadily increasing membership strongly indicates the broad interest in and need for this type of service.

H. P. Kramer

H. P. Kramer
Chief, Training Program

ANALYTICAL REFERENCE SERVICE MEMBERS*

STATE AGENCIES

Alabama Water Improvement Commission
Arizona State Department of Health
Arkansas State Board of Health
California State Department of Public Health (Berkeley)
California State Department of Public Health (Los Angeles)
California Department of Water Resources
California Disaster Office
Colorado State Department of Public Health
Connecticut State Department of Health
Delaware Water Pollution Commission
Florida State Board of Health (Bureau of Laboratories, Jacksonville)
Florida State Board of Health (Sanitary Engineering, Jacksonville)
Florida State Board of Health (Pensacola)
Florida State Board of Health (Winter Haven)
State of Hawaii Department of Health
Idaho Department of Health
Illinois State Department of Public Health (Chicago)
Illinois State Department of Public Health (Springfield)
Illinois State Water Survey Division
Indiana State Board of Health
Kansas State Board of Health (Sanitary Engineering Laboratories)
Kentucky State Department of Health
Louisiana State Board of Health
Maryland State Department of Health
Maryland State Water Pollution Control Commission
Massachusetts Department of Public Health
Massachusetts General Hospital
Michigan State Department of Health
Michigan Water Resources Commission
Minnesota State Department of Health
Missouri Department of Public Health and Welfare
Montana State Board of Health
Nebraska State Department of Health
Nevada State Department of Health (Las Vegas)
Nevada State Department of Health (Reno)
New Hampshire State Department of Health
New Jersey Department of Health
New Mexico State Department of Public Health

*October, 1961

New York State Department of Health
New York State Conservation Department
North Carolina Department of Water Resources
Ohio State Department of Health
Oklahoma State Department of Health
Oregon State Board of Health
Pennsylvania Department of Health
Rhode Island Department of Health
South Carolina Water Pollution Control Authority
South Dakota Department of Health
Tennessee Stream Pollution Control Board
Texas State Department of Health
Utah State Department of Health
Vermont State Department of Health
Vermont State Water Conservation Board
Virginia State Department of Health
Virginia State Water Control Board
Washington State Department of Health
West Virginia State Water Resources Commission
Wisconsin State Board of Health

MUNICIPAL AGENCIES

Metropolitan Water District of Southern California
Los Angeles Department of Water and Power
Los Angeles County Flood Control District
Los Angeles Department of Public Works (Hyperion Treatment Plant)
City of Pasadena
Chicago Department of Water and Sewers
Topeka, Kansas Water Works
Flint Water Plant, Department of Public Works and Utilities
St. Louis County Water Company
St. Louis Department of Health and Hospitals
Metropolitan Utilities District (Omaha, Nebraska)
City of Durham Department of Water Resources (North Carolina)
Dayton Department of Service and Buildings
Philadelphia Suburban Water Company
Philadelphia Water Department (Torresdale and Belmont Laboratories)
Philadelphia Department of Public Health

FEDERAL AGENCIES

Food and Drug Administration, Division of Pharmacology, Washington, D. C.
Tennessee Valley Authority, Wilson Dam, Alabama (Occupational Health Branch)
Tennessee Valley Authority, Chattanooga, Tennessee (Stream Pollution Control)
2794th U. S. Air Force Dispensary - Class B

U.S. Army Environmental Hygiene Agency, Maryland
U.S. Dept. of the Interior, Geological Survey, Sacramento, California
U.S. Dept. of the Interior, Geological Survey, Denver, Colorado
U.S. Dept. of the Interior, Bureau of Reclamation, Denver, Colorado
U.S. Dept. of the Interior, Geological Survey, Columbus, Ohio
U.S. Dept. of the Interior, Geological Survey, Philadelphia, Pennsylvania
Pearl Harbor Naval Shipyard
DHEW, PHS Great Lakes - Illinois River Basin Project
DHEW, PHS Off-Site Radiological Safety Program, Las Vegas, Nevada

UNIVERSITIES

Case Institute of Technology, Dept. of Civil and Sanitary Engineering
Columbia University
Georgia Institute of Technology, Dept. of Applied Biology
University of Pittsburgh, Graduate School of Public Health
Purdue University, Department of Chemistry
Rutgers University, Department of Sanitation

INDUSTRY

American Cyanamid Company, Bound Brook, New Jersey
Atlantic Refining Company, Philadelphia, Pennsylvania
Battelle Memorial Institute, Columbus, Ohio
California Water Service Company, San Jose, California
Central Farmers Fertilizer Company, Montpelier, Idaho
Culligan, Inc., Northbrook, Illinois
Dearborn Chemical Company, Chicago, Illinois
E.I. du Pont de Nemours & Co., Aiken, South Carolina
Ekroth Laboratories, Inc., Brooklyn, New York
Food Machinery & Chemical Corp., Pocatello, Idaho
Goodyear Atomic Corporation, Portsmouth, Ohio
Hagan Chemicals & Controls, Inc., Pittsburgh, Pennsylvania
Industrial Chemicals, Inc., South Bend, Indiana
Ionics, Incorporated, Cambridge, Massachusetts
Kennecott Copper Corporation, Salt Lake City, Utah
Monsanto Chemical Company, St. Louis, Missouri
NALCO Chemical Company, Chicago, Illinois
Radiation Detection Company, Palo Alto, California
Reynolds Electrical & Engineering Co., Las Vegas, Nevada
Roy F. Weston, Inc., Newtown Square, Pennsylvania
Sandia Corporation, Sandia Base, Albuquerque, New Mexico
Tracerlab, Inc., Richmond, California

FOREIGN

Vancouver, B.C., Department of National Health & Welfare
Ottawa, Ontario, Department of National Health & Welfare
Ottawa, Ontario, Occupational Health Division, Department of National Health & Welfare

PARTICIPANTS IN THIS STUDY

Arizona State Department of Health
California State Department of Public Health (Berkeley)
California State Department of Public Health (Los Angeles)
California Department of Water Resources
Connecticut State Department of Health
Florida State Board of Health (Bureau of Laboratories, Jacksonville)
Florida State Board of Health (Sanitary Engineering, Jacksonville)
Florida State Board of Health (Sanitary Engineering, Winter Haven)
Illinois State Department of Public Health (Springfield)
Illinois State Water Survey Division
Indiana State Board of Health
Louisiana State Board of Health
Michigan State Department of Health
Minnesota State Department of Health
Montana State Board of Health
New Hampshire State Department of Health
New Jersey Department of Health
New Mexico State Department of Public Health (Contract Lab.)
New York State Department of Health
New York State Conservation Department
North Carolina Department of Water Resources
Pennsylvania Department of Health
South Dakota Department of Health
Tennessee Stream Pollution Control Board
Texas State Department of Health
Utah State Department of Health
Vermont State Department of Health
Virginia State Department of Health
Washington State Department of Health
West Virginia State Water Resources Commission
Wisconsin State Board of Health
Metropolitan Water District of Southern California
Los Angeles Department of Water and Power
Los Angeles County Flood Control District
Chicago Department of Water and Sewers
Flint Water Plant, Department of Public Works and Utilities
St. Louis County Water Company
Philadelphia Suburban Water Company
Philadelphia Water Quality Control and Research Division - Belmont Lab.
Philadelphia Water Quality Control and Research Division - Torresdale Lab.
Tennessee Valley Authority, Chattanooga, Tennessee (Stream Pollution Control)

U.S. Army Environmental Hygiene Agency, Maryland
U.S. Department of the Interior, Bureau of Reclamation, Denver, Colorado
U.S. Department of the Interior, Geological Survey, Sacramento, California
U.S. Department of the Interior, Geological Survey, Denver, Colorado
U.S. Department of the Interior, Geological Survey, Columbus, Ohio
U.S. Department of the Interior, Geological Survey, Philadelphia, Pennsylvania
Sanitary Engineering Division, 13th Naval District, Seattle, Washington
Case Institute of Technology, Dept. of Civil and Sanitary Engineering
University of Pittsburgh, Graduate School of Public Health
American Cyanamid Company, Bound Brook, New Jersey
California Water Service Company, San Jose, California
Dearborn Chemical Company, Chicago, Illinois
Goodyear Atomic Corporation, Portsmouth, Ohio
Industrial Chemicals, Inc., South Bend, Indiana
Sandia Corporation, Sandia Base, Albuquerque, New Mexico
Vancouver, B.C., Department of National Health & Welfare
Ottawa, Ontario, Department of National Health & Welfare

SAMPLES ON WHICH REPORTS HAVE BEEN COMPLETED

Water, Minerals	- Analyzed for calcium, magnesium, hardness, sulfate, chloride, alkalinity, nitrite, nitrate, sodium and potassium. Studies were completed in 1956, 1958 and 1961.
Water, Metals	- Analyzed for copper, cadmium, aluminum, chromium, iron, manganese, and zinc. A study was completed in 1957 and a repeat study is in the report stage and will be completed in 1961.
Water, Fluoride	- Analyzed for fluoride in the presence and absence of interferences with and without distillation, using a specified procedure. Studies were completed in 1958 and 1961.
Water, Radiological	- Analyzed for gross beta and gamma activity. Studies were completed in 1959 and 1961.
Water, Surfactant	- Analyzed for surfactant in various waters. A study was completed in 1959.
Water, Oxygen Demand	- Analyzed for biochemical oxygen demand and chemical oxygen demand. A study was completed in 1960.
Air, Inorganics	- Analyzed for chloride, sulfate, fluoride and nitrate in aqueous solution and on glass fiber hi-vol filter mats. A study was completed in 1958.

SAMPLES NOW UNDER STUDY

Air, Lead	- Analyzed for lead. Report is now being prepared.
Water, Metals	- Analyzed for copper, cadmium, aluminum, chromium, iron, manganese, zinc, and lead. Report is now being prepared.
Water, Trace Elements	- To be analyzed for arsenic, boron, selenium and beryllium.

WATER - MINERALS No. 3

PURPOSE OF THE STUDY

The Water-Minerals No. 3 sample was similar in composition to samples Type I and Type I-A. It was offered at the request of a number of Analytical Reference Service members to provide opportunity for comparison of individual laboratory results, for further evaluation of current procedures, and for the expression of professional opinions regarding these methods.

Interpretation of the results of the previous samples suggested that certain procedures were preferable to others. For example, electrometric endpoint for alkalinity measurements and chloride correction for nitrate determinations were strongly indicated. Discussion and interpretation of the results of this study are given in appropriate sections of this report.

PREPARATION OF SAMPLE

Substrate: Distilled water which had been passed through a deionizing column.

Chemicals: All reagents of ACS reagent grade which were taken from newly opened bottles.

Composition: Sample Water-Minerals No. 3, consisted of 180 liters of substrate containing carefully measured portions of calcium sulfate, magnesium chloride, sodium nitrite, potassium nitrate, and sodium bicarbonate to give the following concentrations:

Total Hardness (as $CaCO_3$)	610	mg/l
Alkalinity (as $CaCO_3$)	42.5	mg/l
Calcium	108	mg/l
Magnesium	82	mg/l
Sulfate	259	mg/l
Chloride	241	mg/l
Nitrite Nitrogen	0.25	mg/l
Nitrate Nitrogen	1.1	mg/l
Sodium	19.9	mg/l
Potassium	3.1	mg/l

Repeated analyses in this laboratory showed no loss of nitrite nor of nitrate nitrogen, nor any gain or loss of alkalinity.

SIGNIFICANCE OF THE STATISTICS

In this study, the 69 participating laboratories reported a total of 1629 analytical results based upon measurements in triplicate.

For convenience, the average value of each determination as reported is tabulated with the deviation from the amount added. The significance of these statistics were discussed in the report on Sample Type II (July, 1957).

The standard deviations were calculated by using the difference between the reported averages and the amount of material actually added. All reported values greater than two standard deviations were then eliminated and the standard deviation recalculated. This "refined" standard deviation more nearly reflects the accuracy of the analytical methods used, since approximately 95% of the data is retained but gross errors stemming from incorrect dilution factors, etc., are discarded.

It should be remembered that the standard deviations reported here are a function of concentration. If the amount of material being measured were halved or doubled, the standard deviation probably would vary depending upon the changes required or affected by the new concentration.

In order that the accuracy of the methods be related more directly to the laboratories performing the determinations, the term "50% range" again is used (Report on Sample Type II, July 1957). This range is defined as the maximum deviation from the amount of material added for the better half (50%) of all results for each measurement. For example, on the calcium determination, the range for 63 laboratories was 196 mg/l, but 32 (50%) laboratories reported values within 3 mg/l of the true figure. The 3 mg/l represents the range within which most of the results will fall. Conversely, any laboratory whose results do not differ from the amount added by more than the 50% range has performed as well as, or better than, half of the participants for that particular determination.

To contain the size of this report within reasonable limits, the comments by participants which merely describe standard procedures are omitted. Only descriptions of method modification or of unusual techniques are included.

DISCUSSION AND COMMENTS

CALCIUM (108 mg/l)

Sixty-three laboratories performed the calcium measurement. Of these, 45 used some modification of the EDTA titration, 5 used the permanganate titration, and the remaining 13 used gravimetric, flame, or unspecified procedures. Most methods gave excellent results, 50% falling within ± 3 mg/l of the added amount. All but 9 of the results were within 1 standard deviation. The average was 112 mg/l and the median value was 107 mg/l.

For the EDTA procedures, the standard deviation was 9.8 mg/l; the volumetric permanganate method was 3.7 mg/l. The latter, however, was based on only 5 results. The 4 results obtained by the gravimetric procedure had a standard deviation of 4.5 mg/l.

While the EDTA method appears to give less accurate results than the other procedures, it should be noted that several widely divergent results had a pronounced effect on the standard deviation. The generally good results obtained by the EDTA procedures, together with their simplicity and speed, may constitute a basis for recommending them as a standard method.

SUMMARY OF CALCIUM ANALYSES

Amount added	108 mg/l
Average deviation from amount added	± 10.9 mg/l
Standard deviation from amount added	± 9.3 mg/l
50% range	± 3.0 mg/l
Method most commonly used	EDTA
Total number of observations	63

LABORATORY COMMENTS ON CALCIUM METHODS

No. 6
This is a very good method but time consuming.

No. 7
End point difficult

No. 8
Gravimetric determination was 1 mg/l lower.

No. 16
The method currently used for routine analysis is the Volumetric (Permanganate) method with overnight digestion at approximately 90°C. Then, titrating with the permanganate a little slower (55° - 60°C), the end point is more persistent. Routinely, a 500 ml sample is used, but in this instance only a 250 ml aliquot could be used in order to obtain triplicate values.

No. 17
Rapid and sufficiently accurate.

No. 19
End point difficult to see when no further color change should occur.

No. 21
It has been found in this laboratory that preliminary neutralization of the total alkalinity and removal of CO_2 gives more stable end points.

No. 25
Too much variation in individual readings. Background too high.

No. 27
Not run in this laboratory.

No. 30
For routine work an EDTA method would be preferable. Although gravimetric is usually more accurate than the volumetric method, we use the volumetric method routinely.

No. 32
Two samples were titrated using murexide. No difficulty was experienced. An additional sample was run using Calcon indicator, with polyvinyl alcohol to reduce the adsorption of the indicator. Slightly higher results were obtained using the latter.

No. 35
We use the cyclohexanediaminetetracetic acid method using murexide as the indicator. The method is no better than the standards which can be used against it. We exert most of our effort in the direction of maintaining good standards. The end points are generally quite specific.

The same problem applies even more specifically in the case of flame spectrophotometry.

No. 36
It is reliable and does not require standards to be run each time. Probably not too satisfactory when small amounts are present and platinum crucibles not available.

No. 37
This method is quite satisfactory for most natural waters. Some difficulty has been experienced with strongly acid waters as well as colored waters.

No. 38
If the filtrate from the calcium determination is saved for the magnesium, the 50 ml of ammonium oxalate recommended by Standard Methods seems to be excessive. We use 5 ml of the ammonium oxalate solution.

No. 39
We could not obtain consistent results because our muffle furnace has no way of measuring or controlling temperature.

No. 42
Method rapid and sufficiently accurate for routine purposes. End point difficult without practice.

No. 46
We are presently using the Versenate method, with "Calcon" as indicator. End point is sharp and distinct. Method appears as accurate as gravimetric; rapid; easily done.

No. 49
Method with murexide is much quicker and requires a smaller sample than the oxalate method which we used until recently. Do not feel it is as accurate as oxalate method.

No. 54
The end point is rather vague and experience is required to duplicate results.

Table 1. CALCIUM (Amount added - 108 mg/l)

Lab. No.	Results	Mean	% dev. within labs.	% dev. from amt. added	Method
SEC	106 108 109	108	0.93	0.93	Calcein Ind. EDTA
1	113 113 113	113	0.00	0.46	Calcein Ind. EDTA
2	110 106 106	107	1.56	1.85	Murexide Ind. EDTA
3	110 110 110	110	0.00	1.85	EDTA
4	102 102 102	102	0.00	5.56	EDTA
5	106 107 108	107	0.63	0.93	EDTA
6	105 105 105	105	0.00	2.78	Volumetric Permanganate
7	270 280 280	279	1.31	156.0	Ammonium Purpurate EDTA
8	104 104 104	104	0.00	3.70	Murexide Ind. EDTA
9	94 86 94	91	4.03	15.50	EDTA
10	104 104 112	107	3.43	3.70	EDTA
11	99 100 100	100	0.33	7.74	Murexide Ind. EDTA
12	111 112 107	110	1.82	2.47	Murexide Ind. EDTA
13	100 100 100	100	0	7.41	EDTA
14	105 106 104	105	0.64	2.78	Volumetric Permanganate
15	107 109 108	108	0.62	0.62	Cal Red Ind. EDTA
16	98 109 107	105	4.12	3.70	Volumetric Permanganate
17	108 108 108	108	0	0	EDTA
18	104 104 104	104	0	3.70	EDTA
19	104 100 100	101	1.98	6.48	EDTA

20	108 108 108	108	0.00	0.00	Calcein Ind. EDTA	30A	109 108 107	108	0.62	0.62	Gravimetric
21	115 111 110	112	1.79	3.70	EDTA	30B	118 105 105	109	5.20	4.93	Volumetric
22	108 108 ---	108	0.00	0.00	Murexide Ind. EDTA	31	100 100 100	100	0	8.00	Murexide Ind. EDTA
23	--- --- ---	---	---	---	---	32	110 107 106	108	1.55	1.55	Murexide Ind.
24	275 275 278	276	0.36	155.50	Murexide Ind. EDTA	33	102 104 104	103	0.97	4.33	Volumetric Permanganate
25	82 86 87	85	2.35	21.29	Flame Spectrophotometer	34	147 150 152	150	1.11	38.58	EDTA
26A	108 108 108	108	0.00	0.00	Calcein Ind. EDTA	35A	130 --- ---	130	0.00	20.37	Murexide Ind. EDTA
26B	--- --- ---	---	---	---	---	35B	129 --- ---	129	0.00	19.44	Flame
27	--- --- ---	---	---	---	---	36	106 110 111	109	1.84	2.16	Gravimetric
28A	96 96 96	96	0.00	11.11	EDTA	37	110 110 108	109	0.92	1.23	Murexide Ind. EDTA
28B	--- --- ---	---	---	---	---	38	105 104 105	105	.31	3.08	Volumetric Permanganate
29	104 104 105	104	0.32	3.40	---	39	104 104 108	105	1.59	2.47	Gravimetric

40	104 104 103	104	0.32	4.01	EDTA	50	98 104 ---	101	2.97	6.48	EDTA
41	104 104 101	103	1.29	4.63	---	51A	103 103 103	103	0.00	4.63	EDTA
42	108 106 107	107	0.63	0.93	Cal Ver I Ind. EDTA	51B	110 108 110 109	109	0.69	1.16	EDTA Murexide
43	99 100 ---	100	0.50	7.87	Murexide	51C	110 105 110	108	2.16	2.16	EDTA Murexide
44A	116 117 116	116	0.28	7.71	Gravimetric	51D	112 114 112	113	0.88	4.32	EDTA
44B	--- --- ---	---	---	---	---	51E	108 108 107	108	0.31	0.31	EDTA Murexide
45	101 106 104	104	1.61	4.01	EDTA Borate-Buffer	52	--- --- ---	---	---	---	---
46	98 100 100	99	1.01	7.71	EDTA Calon Ind.	53	106 107 106	106	0.31	1.55	---
47	104 106 106	105	0.95	2.47	EDTA	54	106 106 106	106	0.00	1.85	EDTA Murexide
48A	102 102 101	102	0.32	5.86	---	55	104 104 104	104	0.00	3.70	EDTA Murexide
48B	109 106 ---	108	1.39	1.39	---	56	109 108 108	108	0.31	0.31	EDTA Ammonium Purpurate
49	103 104 101	103	0.97	4.94	EDTA Murexide						

	81				
57.	85	83	1.60	23.14	EDTA
	83				
	108				
59	111	109	0.92	1.23	---"
	109				

Average of the means	112
Mean % deviation within labs	0.95
Mean % deviation from amount added	10.04
Median	107

MAGNESIUM (82 mg/l)

As in the calcium measurement, magnesium is determined in a variety of ways. Since hardness and calcium analyses were also made, 39 groups took advantage of numerical relationships and reported magnesium by calculation. Other methods used included EDTA titration, gravimetric, colorimetric, and flame. The average deviation for all methods was 13.8 mg/l; standard deviation was 8.0 mg/l.

For the actual manipulative procedures, the EDTA method gave a standard deviation of 2.0 mg/l, based on 3 results. The calculated magnesium results had a standard deviation of 7.1 mg/l, and the gravimetric results produced a standard deviation of 6.6 mg/l based on 9 results. It must be remembered that errors, however small, in the calcium and hardness measurements are reflected and magnified in the calculation.

In summary, the three most commonly used methods for magnesium gave excellent results. When it is necessary actually to carry out the determination, the EDTA titration appears to be preferable on the basis of speed, simplicity, and accuracy.

SUMMARY OF MAGNESIUM ANALYSES

Amount added	82	mg/l
Average deviation from amount added	± 13.8	mg/l
Standard deviation from amount added	± 8.0	mg/l
50% Range	± 2	mg/l
Method most commonly used	Calculation	
Total number of observations	62	

LABORATORY COMMENTS ON MAGNESIUM METHOD

No. 1
Calculated from difference between total hardness and calcium content.

No. 6
In comparing the removal of oxalate and ammonium salts method to a single precipitation of the filtrate and washing from calcium determination, I find very little difference if any in the final result.

No. 7
Good end point

No. 10
Computed from calcium and total hardness results.

No. 16
The method currently used for routine analysis is the Gravimetric Method (double precipitation). The same size aliquot was used as for the calcium determination.

No. 25
Unable to obtain any results using flame spectrophotometer.

No. 27
Not run in this laboratory.

No. 30
Photometric method is used in this laboratory for routine work up to 10 ppm Mg. However such a small aliquot is required for a high Mg such as in this sample the error could be quite large. Gravimetric is probably the best result and checks best with EDTA hardness.

No. 31
Had a high dilution in order to read photometrically. This would add to an inherent error.

No. 35
Magnesium is most commonly calculated from determined hardness and calcium. Occasionally we check magnesium by flame photometry but as a rule our checks stand up very well with the calculated results.

Magnesium standards are made from the metal and are as a rule quite accurate.

No. 36
Same comments as for calcium method. It follows easily after the calcium determination. Both these methods are reasonably free from interfering substances.

No. 39
Results may not be too accurate because of muffle furnace.

No. 42
Satisfactory for routine work.

No. 46
Errors appear small enough to be neglected.

No. 49
Important to use exactly the same amounts of Titian Yellow in blank and samples. Dye and Stabilizer solution not stable enough.

Table 2. MAGNESIUM (Amount added - 82 mg/l)

Lab. No.	Results	Mean	% dev. within labs.	% dev. from amt. added	Method
SEC	81	81	0.00	1.22	Calculated
1	86 86 86	86	0.00	4.88	Calculated
2	80 80 82	81	1.23	1.62	Calculated
3	80 80 80	80	0.00	2.44	Titan Yellow
4	82 82 82	82	0.00	0.00	Calculated
5	83 81 81	82	1.22	1.49	Calculated
6	86 86 85	86	0.38	4.48	Gravimetric
7	372 370 370	371	0.27	352.03	Gravimetric
8	82 82 82	82	0.00	0.00	Calculated
9	77 81 77	78	2.14	4.48	Calculated
10	83 83 78	81	2.88	2.44	Calculated
11	86 85 85	85	0.39	4.06	Calculated
12	80 79 82	80	1.25	2.04	Calculated
13	85 85 84	85	0.39	3.26	Calculated
14	90 94 92	92	1.45	12.20	Gravimetric
15	83 83 83	83	0.00	1.22	Calculated
16	81 72 82	78	5.55	4.48	Gravimetric
17	89 97 91	92	3.26	12.60	Calculated
18	102 102 102	102	0.00	24.39	Calculated
19	88 83 87	88	0.38	6.91	Calculated
20	80 80 81	80	0.41	2.04	Calculated

21	77 --- ---	77	0.00	6.10	Calculated	31	59 59 59	59	0.00	28.05	Brilliant Yellow Photometric
22	81 82 ---	81	0.62	0.61	Calculated	32	82 81 80	81	0.83	1.22	Calculated
23	--- --- ---	---	---	---	---	33	83 83 83	83	0.00	1.22	Gravimetric
24	354 354 351	353	0.38	330.48	Calculated	34	58 57 56	57	1.18	30.49	Calculated
25	--- --- ---	---	---	---	---	35A	64 --- ---	64	0.00	21.95	Calculated
26A	83 83 83	83	0.00	1.22	Calculated	35B	64 --- ---	64	0.00	21.95	Flame
26B	--- --- ---	---	---	---	---	36	82 79 79	80	1.66	2.44	Gravimetric
27	--- --- ---	---	---	---	---	37	80 80 80	80	0.00	2.44	Calculated
28	87 87 87	87	0.00	6.10	Calculated	38	84 82 82	83	1.20	0.82	EDTA
29	81 82 81	81	0.41	0.82	---	39	94 94 93	94	0.35	14.23	Gravimetric
30A	84 84 84	84	0.00	2.44	Gravimetric	40	88 86 87	87	0.77	6.10	Calculated
30B	75 79 76	76	1.75	6.50	Photometric	41	86 82 84	84	1.58	2.44	---

42	79 80 79	79	0.42	3.26	Calculated	51B	85 86 84	85	0.79	3.66	Versenate Eriochrome Black-T
43	86 85 ---	85	0.59	4.27	Calculated	51C	82 83 81	82	0.82	0.82	Calculated
44A	87 89 88	88	0.76	7.32	Gravimetric	51D	78 78 78	78	0.00	4.88	Calculated
44B	--- --- ---	---	---	---	---	51E	80 81 80	80	0.41	2.04	Versenate Eriochrome Black-T
45	60 55 53	56	4.77	31.71	Colorimetric	52	--- --- ---	---	---	---	---
46	85 84 86	85	0.79	3.66	Calculated	53	82 --- ---	82	0.00	0.00	Calculated
47	83 84 83	83	0.40	1.62	Calculated	54	83 83 82	83	0.40	0.82	Calculated
48A	76 76 74	75	1.33	8.13	---	35	83 83 83	83	0.00	1.22	Calculated
48B	82 82 ---	82	0.00	0.00	---	56	82 82 82	82	0.00	0.00	Calculated
49	83 82 81	82	0.82	0.82	Photometric	57	74 72 73	73	0.92	10.98	Calculated
50	96 89	92	3.80	12.80	Calculated	59	84 84 84	84	0.00	2.44	---
51A	82 81 82	82	0.40	0.40	Calculated						

Average of the means	90.3
Mean % deviation within labs	8.51
Mean % deviation from amount added	16.82
Median	82

CHLORIDE (241 mg/l)

Many methods are employed for chloride determination. Forty-two laboratories reported results based on the Mohr titration and 9 on the mercuric nitrate procedure. Other laboratories reported using the Volhard, turbidimetric, and gravimetric procedures.

For the Mohr method, the standard deviation was 10.0 mg/l. The mercuric nitrate gave slightly better results, with a standard deviation of 7.8 mg/l. Half of the results, regardless of method used, fell within ± 6 mg/l of the known value.

SUMMARY OF CHLORIDE ANALYSES

Amount added	241 mg/l
Average deviation from amount added	± 10.5 mg/l
Standard deviation from amount added	± 11.3 mg/l
50% Range	± 6.0 mg/l
Method most commonly used	Mohr
Total number of observations	63

LABORATORY COMMENTS ON CHLORIDE METHOD

No. 1
Used aliquots of 50, 20, and 10 ml respectively.

No. 6
The end point can be detected better by titrating in yellow light (bug lamp).

No. 7
End point poor until sample diluted.

No. 12
End point viewed under yellow light.

No. 13
Some people seem to have difficulty detecting the end point in this titration. However, most of our technicians are able to get good precision.

No. 15
Direct reading potentiometric method using silver-silver chloride electrode, as described by Stern and Shwachman, Analytical Chemistry, Vol. 30, Sept. 1958, p. 1506. We use a Beckman zeromatic pH meter to determine the potential between electrodes, substituting a 2000 ohm resistor for the thermo compensator to increase sensitivity.

No. 16
I find it superior to the other two methods because of the sharpness of the end point determination.

No. 17
Aliquots of 5, 10, and 25 ml of sample used with results being progressively higher. This is probably due to the white silver chloride making the brown end point more difficult to detect. This problem is not so great in samples of lower chloride concentration.

No. 18
This method is satisfactory although considerable experience is required in order to detect the end point. For more than six years this method has been used successfully in our laboratory.

No. 24
Yellow light used for titration.

No. 25
End point is sometimes hard to be sure of.

No. 26
Samples are titrated under a yellow light to aid in detecting the end point.

No. 32
It is the practice of this laboratory to run chlorides after the alkalinity determination. No correction is made for pH, and all samples are titrated over a light beam for better detection of end point.

No. 35
We use the standard Mohr method for chloride estimation and are very satisfied with it.

No. 36
Believe Mohr method superior to Volhard method so far as end point is concerned. Used Mohr method, Method B.

No. 37
This method is quite satisfactory for most natural waters. Some difficulty has been experienced with strongly acid waters as well as colored waters.

No. 38
The xylene cyanol FF modification had been tried in the past. Although the end point is slightly sharper, the indicator with the xylene cyanol is not stable.

No. 42
Method straightforward and simple. Sharp end point.

No. 46
Mercuric nitrate method used. End point superior to Mohr method.

No. 47
The Mohr method is preferred due to the stability of the reagents.

No. 49
Consistent results achievable using blank and indicator references to titrate against.

Table 3. **CHLORIDE** (Amount added - 241 mg/l)

Lab. No.	Results	Mean	% dev. within labs.	% dev. from amt. added	Method
SEC	235 235 235	235	0.00	2.49	Mercuric Nitrate
1	236 235 237	236	0.28	2.07	Mohr
2	240 240 250	243	1.78	1.52	Mohr
3	234 235 236	235	0.29	2.49	Mercuric Nitrate
4	232 233 231	232	0.29	3.73	Electric Titrimeter
5	222 222 222	222	0.00	7.88	Mohr
6	242 242 242	242	0.00	0.41	Mohr
7	245 242 240	242	0.69	0.83	Mohr
8	238 238 238	238	0.00	1.24	Murexide
9	240 240 235	238	0.98	1.11	Mohr
10	230 230 235	232	1.00	3.87	Mohr
11	235 235 235	235	0.00	2.49	Mohr
12	240 238 232	237	1.27	1.80	Mohr
13	240 240 240	240	0.00	0.41	Mohr
14	226 226 228	227	0.44	6.64	Turbidimetric
15	238 238 238	238	0.00	1.24	pH Meter
16	211 211 209	210	0.48	12.73	Mercuric Nitrate
17	225 239 216	227	3.67	5.95	Silver Nitrate Titration-Potassium Chromate Ind.
18	244 243 242	243	0.28	0.83	Mohr
19	248 247 246	247	0.27	2.49	Mohr

20	235 233 234	234	0.29	2.90	---	30A	231 231 231	231	0.00	4.15	Mohr
21	238 --- ---	238	0.00	1.24	Mohr	30B	--- --- ---	---	---	---	---
22	229 227 228	228	0.29	5.39	Mercuric Nitrate Diphenylcarbazone Ind.	31	239 240 237	239	0.42	0.97	Mohr
23	219 232 230	227	2.35	5.81	Conductometric Titration	32	239 239 238	239	0.14	0.97	Mohr
24	291 293 292	292	0.23	21.16	Mohr	33	235 235 236	235	0.14	2.35	Mohr
25	240 240 236	238	0.84	0.97	Mohr	34	233 233 233	233	0.00	3.32	Mercuric Nitrate
26A	234 233 233	233	0.14	3.18	Mohr	35A	230 --- ---	230	0.00	4.56	Mohr
26B	--- --- ---	---	---	---	---	35B	--- --- ---	---	---	---	---
27	213 213 213	213	0.00	11.61	Volhard	36	234 238 234	235	0.71	2.35	Mohr
28A	230 232 228	230	0.58	4.56	Mohr	37	230 232 228	230	0.87	4.56	Mohr
28B	--- --- ---	---	---	---	---	38	232 236 235	234	0.71	2.77	Mercuric Nitrate
29	230 234 232	232	0.57	3.73	---	39	258 230 272	253	6.19	8.14	Mohr

40	239 236 239	238	0.56	1.24	Mohr	50	264 262 263	263	0.25	9.12	Mohr
41	320 320 320	320	0.00	32.78	---	51A	236 235 236	236	0.14	2.21	Mohr
42	235 232 232	233	0.57	3.32	Mercuric Nitrate	51B	234 236 235 236	235	0.32	2.39	Mohr
43	237 240 ---	238	0.63	1.03	Mohr	51C	236 237 238	237	0.28	1.66	Automatic Titrator Mohr
44A	227 227 227	227	0.00	5.81	Mohr	51D	210 210 210	210	0.00	12.86	Mohr
44B	--- --- ---	---	---	---	---	51E	233 236 232	234	0.71	3.04	Mohr
45	220 215 212	216	1.39	10.51	Mohr	52	244 244 244	244	0.00	1.24	Mercuric Nitrate
46	245 240 240	242	0.96	0.83	Mercuric Nitrate	53	220 221 224	222	0.75	8.02	Mohr
47	235 238 238	237	0.56	1.66	Mohr	54	243 245 243	244	0.41	1.11	Mohr & Mercuric Identical
48A	236 235 235	235	0.14	2.35	Potentiometric	55	236 238 236	237	0.42	1.80	Mohr
48B	--- --- ---	---	---	---	---	56	231 236 234	233	0.86	3.04	Mohr
49	227 227 226	227	0.15	5.95	Mohr						

	244						
57	244	243	0.41	0.97	Mohr		
	242						
	227						
59	227	227	0.00	5.81	---		
	227						

Average of the means	237
Mean % deviation within labs.	0.57
Mean % deviation from amount added	4.37
Median	235

SULFATE (259 mg/l)

A variety of techniques are employed in the sulfate determination, but the gravimetric procedure remains the most commonly used. Sixty-five results were reported, of which 32 were obtained by the gravimetric analysis, 19 by the turbidimetric, and 14 by the Thorin, THQ, Barium Chloranilate, by unidentified titrimetric procedures, and unspecified methods.

The arithmetic mean for all methods was 249 mg/l with an average deviation of 21.9 mg/l and a standard deviation of 22.9 mg/l.

The standard deviations for the gravimetric and turbidimetric methods were 11.9 and 23.9 mg/l, respectively. The turbidimetric results show a decided improvement over the results of the previous Water-Minerals ARS sample which had a standard deviation of 32.1 mg/l from a true value of 288 mg/l. This improvement may indicate that increased experience with the technique can bring accuracy to a level satisfactory for routine use, enabling the analyst to utilize the speed and simplicity of the turbidimetric procedure.

SUMMARY OF SULFATE ANALYSES

Amount added	259 mg/l
Average deviation from amount added	± 21.9 mg/l
Standard deviation from amount added	± 22.9 mg/l
50% range	± 7 mg/l
Method most commonly used	Gravimetric
Total number of observations	65

LABORATORY COMMENTS ON SULFATE METHOD

No. 6
Seeding the hot sample with 3 or 4 drops of barium chloride solution about 2 or 3 minutes before adding the excess of hot barium chloride solution seems to provide a coarser precipitate. An aged solution of barium chloride also seems to aid in providing a coarse precipitate.

No. 7
Very satisfactory

No. 10
Time consuming but results are satisfactory.

No. 18
Although the gravimetric method might be considered time consuming, results are usually reliable and rarely need to be repeated.

No. 20
Turbidimetric method using Sulfa Ver Powder by Hach, otherwise as in the 10th Edition S. M. Hach reagent is used since it appears that with this reagent the time element is not so critical.

No. 25
Cumbersome

No. 28
First time the turbidimetric method has been used in laboratory.

No. 31
Tedious process but still the most trustworthy.

No. 35
We used the regular gravimetric procedure except that we remove interferences using exchange resins. We use large amounts of ammonium chloride. The resin and ammonium chloride seems to almost completely inhibit coprecipitation.

No. 36
It is reliable and does not require standards to be run each time. Probably not too satisfactory when small amounts are present and platinum crucibles are not available.

No. 37
Difficulties due to color fading have been experienced with the Thorin indicator. Color fading of the Thorin indicator on standing had presented some difficulties. This has been overcome by preparing the Thorin in smaller quantities.

No. 38
Of the routine determinations normally performed in our laboratory, the gravimetric sulfate is one of the most time consuming. We continue to use this method in lieu of a more satisfactory procedure.

No. 42
Best method for routine analysis. Must adhere to strict timing and stirring. Dilution factor a problem with high sulfate concentration.

No. 45
Turbidimetric method found less laborious and just as accurate.

No. 47
Thorin method most satisfactory for routine work.

No. 49
Results not consistent.

No. 54
The sample was passed through an anionic resin column. The pH was adjusted to 3. 3, THQ added as indicator and titrated with $BaCl_2$. We realize that this is not a superior method for the SO_4 determination, but we do feel that the results are within reason and are accurate enough for our work.

No. 57
Hellige Nephelometer used and preferred to spectrophotometer.

Table 4. SULFATE (Amount added - 259 mg/l)

Lab. No..	Results	Mean	% dev. within labs.	% dev. from amt. added	Method
SEC	260 252 260	257	1.43	1.16	Turbidimetric
1	263 264 264	264	0.13	1.80	Gravimetric
2	250 253 253	252	0.53	2.70	Thorin
3	259 260 260	260	0.13	0.26	Gravimetric
4	255 255 256	255	0.13	1.42	Turbidimetric
5	295 300 305	300	1.11	15.83	Turbidimetric
6	240 242 241	241	0.28	6.95	Gravimetric
7	248 248 240	245	1.50	5.28	Turbidimetric
8	249 250 249	249	0.13	3.73	Turbidimetric
9	315 340 325	327	3.47	26.13	Turbidimetric
10	237 249 250	245	2.31	5.28	Gravimetric
11	244 250 250	248	1.03	4.25	Turbidimetric
12	252 253 253	253	0.13	2.06	Visual Thorin
13	262 269 277	269	1.86	3.99	Gravimetric
14	280 278 276	278	0.48	7.08	Turbidimetric
15	255 255 258	256	0.26	1.16	Turbidimetric
16	264 208 257	243	6.86	7.46	Gravimetric
17	268 288 276	277	2.53	7.08	Gravimetric
18	266 266 267	266	0.12	2.83	Gravimetric
19	265 274 270	269	1.24	1.42	Turbidimetric

20	260 245 250	252	2.25	3.08	Turbidimetric	30A	254 253 256	254	0.39	1.80	Gravimetric
21	256 251 251	253	0.92	2.44	Gravimetric	30B	--- --- ---	---	---	---	---
22	262 260 255	259	1.03	1.03	Gravimetric	31	266 260 258	261	1.14	1.16	Barium, Chloride Gravimetric
23	188 188 188	188	0.00	27.41	Turbidimetric	32	258 257 254	256	0.65	1.03	Gravimetric
24	310 310 307	309	0.43	19.31	Turbidimetric	33	253 254 253	253	0.13	2.19	Gravimetric
25	258 257 258	258	0.13	0.64	Gravimetric	34	223 238 255	239	4.60	7.85	Turbidimetric
26A	260 261 264	262	0.64	1.03	Gravimetric	35A	257 --- ---	257	0.00	0.39	Resin and Gravimetric
26B	--- --- ---	---	---	---	---	35B	257 --- ---	257	0.00	0.39	Gravimetric
27	9.6 9.6 9.6	9.6	0.00	96.29	Titrimetric	36	209 195 197	200	2.84	22.65	Gravimetric
28A	228 245 ---	236	3.72	8.69	Gravimetric	37	272 261 260	261	1.53	2.06	Colorimetric Thorin
28B	265 266 260	264	0.89	1.80	Turbidimetric	38	253 253 249	252	0.66	2.83	Gravimetric
29	234 235 234	234	0.41	9.53	---	39	234 229 245	236	2.54	8.88	Gravimetric

40	326 340 331	332	1.51	28.31	TH Q	50	274 250 263	262	3.18	3.60	TH Q
41	258 264 258	260	0.90	0.90	---	51A	257 262 262	260	0.90	1.03	Gravimetric
42	253 255 257	255	0.65	1.54	Turbidimetric	51B	259 258 259 258	258	0.19	0.19	Gravimetric
43	105 100 ---	102	1.64	60.42	Barium Chloranilate	51C	251 249 247	248	0.67	3.86	Gravimetric
44A	208 206 204	206	0.65	20.46	Titration	51D	262 265 272	266	1.38	2.83	Gravimetric
44B	251 248 250	250	0.40	3.60	Gravimetric	51E	269 255 253	259	2.58	2.58	Gravimetric
45	278 281 275	278	0.72	7.34	Turbidimetric Gravimetric	52	--- --- ---	---	---	---	---
46	253 254 253	253	0.13	2.19	Gravimetric	53	233 236 ---	234	0.11	9.46	Gravimetric
47	264 266 272	267	1.12	3.24	Thorin	54	240 240 242	241	0.41	7.08	Titration with $BaCl_2$ TH Q Ind.
48A	250 251 251	251	0.13	3.24	Turbidimetric	55	257 252 257	254	1.05	1.16	Gravimetric
48B	--- --- ---	---	---	---	---	56	250 290 260	266	5.76	5.28	Turbidimetric
49	258 265 270	264	1.64	2.32	(Turbidimetric) Photometric with Barium Cl						

	135				Turbidimet-		
57	135	135	0.00	47.88	ric Hellige	Average of the means	249
	135				Nephelometer	Mean % deviation within labs	1.17
						Mean % deviation from amount added	8.48
	254					Median	256
59	254	254	0.00	1.93	---		
	254						

HARDNESS (610 mg/l)

Sixty-four results were reported for the hardness determination, of which 56 were obtained by the EDTA titration. The average deviation of only 18 mg/l at a level of 610 mg/l indicates that the method gives excellent results over a wide range of concentrations. Materials which are said to interfere with this procedure, such as iron, aluminum, manganese, or polyphosphates, were not present in the sample so that the accuracy predicted here may be better than that obtained on natural samples. Probably the commonest source of error in this analysis is the aging of Chrome Black T indicator solution. Aging probably would occur in laboratories where hardness determinations are not done on a routine basis.

The standard deviation of 17.4 mg/l indicated a reliable method.

SUMMARY OF HARDNESS ANALYSES

Amount added	610 mg/l (as $CaCO_3$)
Average deviation from amount added	± 18 mg/l
Standard deviation from amount added	± 17.4 mg/l
50% range	± 10 mg/l
Method most commonly used	EDTA with Eriochrome Black T
Total number of observations	64

LABORATORY COMMENTS ON TOTAL HARDNESS METHOD

No. 1
Have noticed unstability of Univer over a prolonged period in field kits. End point is not as true and is reached more quickly.

No. 3
Titian Yellow and Versenate calcium used to report T. H. results. Versenate result higher than Ca + Mg.

No. 7
Good end point.

No. 16
A 50 ml aliquot was used on this sample due to the excessive hardness, and request for triplicate determination.

No. 30
We determined EDTA Hardness - Excellent for routine work. Calculated hardness using gravimetric Mg and gravimetric Ca is 615 ppm. Because of small aliquot used this is not a very large discrepancy.

No. 32
End point was very sharp.

No. 33
We find a rather close correlation between calculation and EDTA Titration.

No. 37
This method has proven satisfactory for most natural and treated waters that are not strongly acid.

No. 42
Method accurate and rapid. Very sharp end point. However this indicator tends to deteriorate rapidly without refrigeration. We have found it necessary to order directly from the manufacturer and request the latest stock.

No. 43
We use Eriochrome Black T in triethanolamine. This gives excellent color change and indicator is stable.

No. 46
End point appears slightly sharper than Eriochrome T.

No. 49
Takes experience to read end point.

No. 54
The EDTA Titration method, using the Na_2S inhibitor was used for the determination. A considerable number of the samples analyzed at this laboratory are highly colored by dye waste, therefore causing trouble with this test as well as the others which are run by indicator change end points. Usually dilution is used as a means of diluting the original sample color.

Table 5. HARDNESS (Amount added - 610 mg/l)

Lab. No.	Results	Mean	% dev. within labs.	% dev. from amt. added	Method
SEC	601 602 602	602	0.05	1.37	EDTA Eriochrome Black T
1	635 635 635	635	0.00	4.10	Univer I EDTA
2	606 594 600	600	0.67	1.64	EDTA Eriochrome Black T
3	604 604 604	604	0.00	0.98	Ca + Mg Calculated
4	595 597 595	596	0.17	2.30	EDTA
5	606 600 604	603	0.39	1.09	EDTA
6	616 616 613	615	0.22	0.82	Calculated
7	651 651 652	651	0.05	6.78	EDTA Borate Buffer
8	595 595 595	595	0.00	2.46	EDTA
9	554 554 554	554	0.00	9.18	EDTA Ammonia Buffer Proc.
10	600 600 600	600	0.00	1.64	EDTA
11	600 600 604	601	0.28	1.42	EDTA Eriochrome Black T
12	610 605 607	607	0.28	0.44	EDTA Eriochrome Black T
13	600 600 596	599	0.28	1.86	EDTA
14	580 580 584	581	0.29	6.33	EDTA Borate Buffer
15	612 614 613	613	0.11	0.49	EDTA - Monethanol Amine HCl Buffer
16	590 618 590	599	2.06	2.07	Ammonia Buffer
17	634 666 645	648	1.80	6.28	EDTA
18	611 611 611	611	0.00	0.16	EDTA
19	609 609 619	612	0.71	0.60	EDTA Borate Buffer

20	597 601 601	600	0.28	1.69	EDTA Ammonia Buffer	30A	602 604 603	603	0.11	1.15	EDTA
21	604 604 582	597	1.62	2.19	EDTA Eriochrome Black T	30B	--- --- ---	---	---	---	---
22	606 613 609	609	0.38	0.44	EDTA Eriochrome Black T	31	614 608 614	612	0.44	0.55	Versenate
23	504 506 504	505	0.20	17.27	EDTA	32	605 603 602	603	0.17	1.09	Versenate Ammonia Buffer
24	628 628 629	628	0.05	3.00	EDTA Borate Buffer	33	598 601 601	600	0.22	1.64	EDTA
25	604 605 603	604	0.11	0.98	EDTA	34	605 609 609	608	0.27	0.38	EDTA Borate Buffer
26A	610 610 610	610	0.00	0.00	EDTA Eriochrome Black T	35A	589 --- ---	589	0.00	3.44	EDTA
26B	--- --- ---	---	---	---	---	35B	587 --- ---	587	0.00	3.77	Flame
27	688 688 688	688	0.00	12.79	EDTA	36	614 612 612	613	0.16	0.44	Ammonia Buffer
28A	600 600 600	600	0.00	1.64	EDTA	37	605 605 605	605	0.00	0.82	(EDTA) Complexo- metric
28B	730 730 730	730	0.00	19.67	Soap Titration	38	611 614 610	612	0.27	0.27	EDTA
29	590 594 592	592	0.22	2.95	---	39	564 560 560	561	0.30	7.98	Ammonia Buffer

40	622 614 616	617	0.49	1.20	---
41	596 602 602	600	0.45	1.64	---
42	600 600 595	598	0.39	1.91	EDTA Monover Ind.
43	600 600 ---	600	0.00	1.64	Versene Borate Ammonia Buffer
44A	590 620 600	603	1.82	2.73	EDTA Univer II Ind.
44B	--- --- ---	---	---	---	---
45	640 650 660	650	1.03	2.19	EDTA
46	600 600 595	598	0.39	1.91	EDTA Calmagite Ind.
47	600 610 605	605	0.55	0.82	EDTA
48A	605 607 605	606	0.17	0.71	EDTA
48B	--- --- ---	---	---	---	---
49	596 596 594	595	0.17	2.40	EDTA
50	644 624 ---	634	1.58	3.93	EDTA
51A	594 592 593	593	0.11	2.79	EDTA
51B	623 623 622 625	623	0.12	2.17	Versenate
51C	610 603 608	607	0.44	0.49	EDTA Borate Buffer
51D	611 612 611	611	0.05	0.21	EDTA
51E	602 605 598	602	0.39	1.37	Versenate
52	--- --- ---	---	---	---	---
53	599 604 606	601	0.55	1.15	EDTA
54	605 605 603	604	0.17	0.93	EDTA
55	600 599 599	599	0.06	1.75	EDTA Eriochrome Black T
56	608 608 608	608	0.00	0.33	EDTA Eriochrome Black T

	508				EDTA		
57	508	509	0.20	16.61	Eriochrome	Average of the means	605
	510				Black T	Mean % deviation within labs	0.33
						Mean % deviation from amount added	2.94
	590					Median	603
59	590	590	0.00	3.28	---		
	590						

NITRITE (0.25 mg/l)

Diazotization was the only method reported by the 49 laboratories that performed the nitrite analysis. The bar charts show that the distribution does not form a normal curve, indicated also by the spread between the mean and median. Although the median value is 0.03 mg/l low, the mean is too high by the same amount, due to 6 inexplicably high results. No correlation is evident between the amount reported and the age of the sample. Thirty-eight results fell within one standard deviation of 0.06 mg/l; half of the analyses were within ± 0.04 mg/l.

SUMMARY OF NITRITE ANALYSES

Amount added	0.25 mg/l
Average deviation from amount added	± 0.09 mg/l
Standard deviation from amount added	± 0.062 mg/l
50% range	± 0.04 mg/l
Method most commonly used	Diazotization
Total number of observations	49

LABORATORY COMMENTS ON NITRITE METHOD

No. 1
Not routine

No. 7
Very satisfactory

No. 10
Compared colorimetrically against permanent standards.

No. 16
No determination in current use in this laboratory due to the age of the samples upon arrival. Also, there was not sufficient sample sent for this determination.

No. 18
This method is sufficiently simple and rapid. Good precision and accuracy have been obtained. Our final readings were obtained with a Model B Spectrophotometer using a wavelength of 520 mμ.

No. 25
Seems good, though I had trouble due to trouble with the phototube in my spectrophotometer.

No. 27
Not run in this laboratory.

No. 30
Excellent for routine work

No. 31
Seemed high but we would never run this analysis on a sample older than 24 hours.

No. 32
Not run

No. 35
We have altered Standard Methods in that we use dimethylalphanaphythylamine in the place of the usual reagent. The method is very sensitive. Great care must be exercised in the preparation and maintenance of standards.

No. 36
Preliminary investigation to get correct dilution for colorimetric work is a necessity here. No chlorine or NCl_3 found with o-tolidine.

No. 37
This method appears to be quite sensitive. It seems that technique and speed are significant in this determination.

No. 42
Not a routine analysis

No. 43
We do not run.

No. 50
Could not get proper color development in sample.

No. 54
The method is easy and doesn't have extensive time requirements.

No. 55
Nitrite not determined.

Table 6. NITRITE (Amount added - 0.25 mg/l)

Lab. No.	Results	Mean	% dev. within labs.	% dev. from amt. added	Method
SEC	0.28 0.28 ---	0.28	0.00	12.00	a-Naphthylamine Diazotization
1	--- --- ---	---	---	---	---
2	0.77 0.78 0.74	0.76	2.20	204.00	Diazotization
3	0.25 0.30 0.30	0.28	8.32	12.00	Diazotization
4	0.22 0.20 0.21	0.21	3.20	16.00	Diazotization
5	0.3 0.3 0.3	0.3	0.00	20.00	Diazotization
6	0.22 0.22 0.21	0.22	1.50	12.00	Diazotization
7	0.21 0.21 0.21	0.21	0.00	16.00	Diazotization
8	0.21 0.22 0.22	0.22	1.50	12.00	Diazotization
9	0.38 0.40 0.40	0.39	2.56	56.00	Diazotization
10	0.20 0.20 0.20	0.20	0.00	20.00	Diazotization
11	0.23 0.23 0.23	0.23	0.00	8.00	Diazotization
12	0.18 0.21 0.22	0.20	8.35	20.00	Diazotization
13	0.20 0.20 0.20	0.20	0.00	20.00	Diazotization
14	0.21 0.21 0.21	0.21	0.00	16.00	Diazotization
15	0.22 0.21 0.22	0.22	1.57	12.00	Diazotization
16	--- --- ---	---	---	---	---
17	0.7 0.7 0.7	0.7	0.00	180.00	Diazotization
18	0.70 0.71 0.71	0.71	0.46	180.00	Diazotization
19	0.25 0.25 0.24	0.25	1.32	1.32	Diazotization

20	0.21 0.22 0.22	0.22	1.50	12.00	Diazotization	30A	0.21 0.21 0.21	0.21	0.00	16.00	Diazotization
21	0.21 0.22 0.21	0.21	1.57	12.00	Diazotization	30B	--- --- ---	---	---	---	---
22	0.20 0.23 ---	0.22	6.82	12.00	Diazotization	31	0.23 0.23 0.24	0.23	1.43	8.00	Diazotization
23	--- --- ---	---	---	---	---	32	--- --- ---	---	---	---	---
24	0.19 0.18 0.18	0.18	1.83	24.00	Diazotization	33	0.23 0.22 0.23	0.23	1.43	8.00	Diazotization Modified
25	0.18 0.21 0.22	0.20	8.35	16.00	Diazotization	34	0.23 0.23 0.22	0.28	1.43	8.00	Diazotization
26A	0.22 0.22 0.22	0.22	0.00	12.00	Diazotization	35A	0.21 0.22 0.22	0.22	1.50	12.00	---
26B	--- --- ---	---	---	---	---	35B	--- --- ---	---	---	---	---
27	--- --- ---	---	---	---	---	36	0.23 0.23 0.23	0.23	0.00	8.00	Diazotization
28A	0.20 0.20 0.25	0.23	11.61	12.00	Diazotization	37	1.0 1.2 0.9	1.0	10.00	312.00	Diazotization
28B	--- --- ---	---	---	---	---	38	0.21 0.21 0.21	0.21	0.00	16.00	Diazotization
29	--- --- ---	---	---	---	---	39	0.29 0.29 0.25	0.28	5.96	8.00	Diazotization

40	--- --- ---	---	---	---	---	49	0.26 0.26 0.26	0.26	0.00	4.00	Diazotization
41	--- --- ---	---	---	---	---	50	--- --- ---	---	---	---	---
42	0.21 0.21 0.21	0.21	0.00	16.00	Diazotization	51A	0.21 0.22 0.22	0.22	1.50	12.00	(Diazotization) 1-Naphylamine
43	--- --- ---	---	---	---	---	51B	0.13 0.19 0.19 0.19	0.17	14.71	20.00	Diazotization
44A	0.22 0.22 0.22	0.22	0.00	12.00	Diazotization	51C	0.21 0.12 0.12	0.15	26.67	40.00	Diazotization
44B	--- --- ---	---	---	---	---	51D	0.26 0.24 0.26	0.25	2.68	4.00	(Diazotization) 1-Naphylamine
45	0.14 0.13 0.16	0.14	7.14	40.00	(Diazotization) Sulfanilic Acid 1-Naphthilamine Colorimetric	51E	0.20 0.20 0.24	0.21	7.95	12.00	Diazotization
46	--- --- ---	---	---	---	---	52	0.61 0.64 ---	0.62	3.23	148.00	Diazotization
47	0.24 0.24 0.24	0.24	0.00	4.00	Diazotization	53	--- --- ---	---	---	---	---
48A	0.21 0.23 0.21	0.22	4.55	12.00	Hellige Comparator	54	0.20 0.19 0.20	0.20	1.65	20.00	Diazotization
48B	--- --- ---	---	---	---	---	55	--- --- ---	---	---	---	---

	---						0.21			
56	---	---	---	---	---	59	0.23	0.22	4.54	12.00	---
	---						0.22			
	0.5									
57	0.5	0.5	0.00	100.00	Diazotization					
	0.5									

Average of the means	0.28
Mean % deviation within labs	3.25
Mean % deviation from amount added	36.11
Median	0.22

NITRATE (1.1 mg/l)

The distribution curve of the nitrate results is similar to the nitrite curve in that the deviations of the high results are of much greater magnitude than those of the low results. The mean value of 2.0 mg/l when compared to the median figure of 1.0 mg/l indicates the abnormal influence of the high results.

Of the 57 reported values for nitrate nitrogen, 40 were obtained by the phenoldisulfonic acid method, 8 by the brucine procedure, and 9 by UV, polarograph, reduction, or unspecified methods. The phenoldisulfonic acid results showed a standard deviation of 1.14 mg/l; the brucine results (a standard deviation) of 0.49 mg/l. The other methods were not used by enough groups to be statistically significant. The phenoldisulfonic acid method evidently leaves much to be desired and does not give reliable results for most operators. The brucine procedure gave generally excellent results. If the 1 value of 28 mg/l, which apparently is due to an arithmetical error, is discarded, the standard deviation for this procedure is reduced to 0.16 mg/l.

SUMMARY OF NITRATE ANALYSES

Amount added	1.1 mg/l
Average deviation from amount added	± 1.29 mg/l
Standard deviation from amount added	± 1.00 mg/l
50% range	± 0.30 mg/l
Method most commonly used	phenoldisulfonic acid
Total number of observations	57

LABORATORY COMMENTS ON NITRATE METHOD

No. 3
The ultra-violet method, absorption at 220 mμ, was used to determine NO_3. The result was corrected for NO_2 interference. (PDA method gave much lower results.)

No. 7
Room for improvement

No. 16
I find that it is the best method stated in the text, except for the complete chloride removal, which can present a problem on various types of waters.

No. 24
KOH used for alkaline reagent gave ppt.

No. 25
Two filtrations seem to me to add to accuracy problems, especially if you are trying to keep volume of sample within 50 ml, I used 100 ml volumes and feel I should have rinsed the filter paper even more. Using a portion of my standard solution, color was still visible on the filter paper after 7 rinsings with distilled water.

No. 26
The alkaline ferrous sulfate method is much faster than the aluminum wire reduction and the results are more reproducible.

No. 27
Not run in this laboratory.

No. 31
We do not have the apparatus for the reduction method and the silver sulfate precipitation gives a false brown hue. We would not run this analysis on a sample older than 24 hours.

No. 32
It was difficult to establish good reference points on the curve.

No. 33
We do not like this method when the presence of high chlorides makes it necessary to remove them prior to evaporation and nitration with phenoldisulfonic acid.

No. 35
We use the phenoldisulfonic acid method except that we use exchange resins to convert the sample to acid form, warm to destroy nitrous acid, neutralize with ammonium hydroxide and then take to dryness over a waterbath. The color is developed in the usual way using ammonia as the neutralizing agent.

No. 36
Interfering chloride very large in this sample. It was removed before running nitrate. Complete removal was checked by adding additional Ag^+ after Ag_2SO_4 ppt was filtered off. Highest answer assumed correct; lower ones assumed due to filtration or digestion losses. Care must be observed to evaporate slowly and to add NH_4OH to cold sample and cap immediately.

No. 37
This method has proven satisfactory for most natural waters.

No. 47
Erratic results can be obtained on natural waters.

No. 49
Brown color with some wastes interfere with readings.

No. 53
Erratic results and no correction since nitrite was not run.

No. 54
The procedure did not work out too well, but it is felt that this was due to our not having the brucine sulfate available. We have brucine crystals on hand and this was used for the test. We feel that this method should give results as good as the phenoldisulfonic acid method.

Table 7. NITRATE (Amount added - 1.1 mg/l)

Lab. No.	Results	Mean	% dev. within labs.	% dev. from amt. added	Method
SEC	1.1 1.1 ---	1.1	0.00	0.00	Phenol Disulfonic Acid
1	0.8 0.8 0.8	0.8	0.00	27.27	Phenol Disulfonic Acid
2	2.0 2.1 2.1	2.1	1.57	87.27	Phenol Disulfonic Acid
3	1.0 1.0 1.0	1.0	0.00	9.09	Ultra Violet 220 mμ
4	0.8 0.9 0.8	0.8	4.13	32.73	---
5	0.1 0.2 0.1	0.1	3.30	87.27	Phenol Disulfonic Acid
6	1.3 1.3 1.3	1.3	0.00	18.18	Phenol Disulfonic Acid
7	0.7 0.7 0.7	0.7	0.00	11.82	Phenol Disulfonic Acid
8	1.0 1.0 1.0	1.0	0.00	9.09	Brucine
9	0.4 0.4 0.4	0.4	0.00	63.64	Phenol Disulfonic Acid
10	1.2 1.0 0.9	1.0	10.00	11.82	Phenol Disulfonic Acid
11	1.4 1.4 1.4	1.4	0.00	27.27	Brucine Sulfate
12	0.5 0.7 0.4	0.6	22.17	50.91	Phenol Disulfonic Acid
13	3.2 2.8 2.9	3.0	5.57	169.09	Phenol Disulfonic Acid
14	0.7 0.7 0.7	0.7	0.00	36.36	Phenol Disulfonic Acid
15	1.0 1.0 1.0	1.0	0.00	9.09	Polarographic
16	0.8 0.8 0.8	0.8	0.00	27.27	Phenol Disulfonic Acid
17	3.1 3.0 3.0	3.0	1.10	96.36	Phenol Disulfonic Acid
18	4.8 4.9 4.8	4.8	0.69	339.09	Phenol Disulfonic Acid
19	1.0 1.2 1.1	1.1	6.09	60.91	Phenol Disulfonic Acid

20	1.0 1.0 1.2	1.1	9.0	9.09	Brucine	30A	1.2 1.2 1.2	1.2	0.00	9.09	Phenol Disulfonic Acid
21	1.3 0.8 0.9	1.0	20.00	20.91	Reduction to NH_3	30B	--- --- ---	---	---	---	---
22	0.8 0.7 ---	0.7	7.14	31.82	Phenol Disulfonic Acid	31	0.4 0.3 0.3	0.3	11.00	69.09	Phenol Disulfonic Acid
23	--- --- ---	---	---	---	---	32	1.4 1.2 1.2	1.3	7.69	15.45	Brucine
24	0.7 0.6 0.6	0.6	5.50	41.82	Phenol Disulfonic Acid	33	3.9 3.7 3.7	3.8	2.63	242.73	Phenol Disulfonic Acid
25	0.8 0.7 0.8	0.8	4.13	30.00	Phenol Disulfonic Acid	34	0.6 0.6 0.7	0.6	5.50	41.83	Phenol Disulfonic Acid
26A	0.9 0.9 0.9	0.9	0.00	18.18	Reduction Std. Meth.	35A	0.4 0.4 0.4	0.4	0.00	63.64	Modified Phenol Disulfonic Acid
26B	0.9 0.9 0.9	0.9	0.00	18.18	Alkaline Ferrous Sulfate	35B	--- --- ---	---	---	---	---
27	--- --- ---	---	---	---	---	36	1.2 1.1 1.3	1.2	5.58	9.09	Phenol Disulfonic Acid
28A	0.9 0.9 0.9	0.9	0.00	18.18	Phenol Disulfonic Acid	37	1.9 1.6 1.9	1.8	7.39	63.64	Phenol Disulfonic Acid
28B	--- --- ---	---	---	---	---	38	1.0 1.0 1.0	1.0	0.00	9.09	Brucine
29	--- --- ---	---	---	---	---	39	0.2 0.2 0.2	0.2	0.00	81.82	Phenol Disulfonic Acid

40	--- --- ---	---	---	---	---
41	--- --- ---	---	---	---	---
42	0.7 0.8 0.8	0.8	4.13	30.00	Phenol Disulfonic Acid
43	--- --- ---	---	---	---	---
44A	0.8 0.6 0.7	0.7	9.57	36.36	Phenol Disulfonic Acid
44B	--- --- ---	---	---	---	---
45	2.8 2.7 2.7	2.7	1.22	145.45	Phenol Disulfonic Acid Colorimetric
46	0.9 0.9 0.9	0.9	0.00	19.09	Phenol Disulfonic Acid
47	0.6 0.9 0.7	0.7	14.29	32.73	Phenol Disulfonic Acid
48A	1.8 --- ---	1.8	0.00	63.64	Hellige Comparator
48B	--- --- ---	---	---	---	---
49	0.84 0.84 0.84	0.84	0.00	23.64	Phenol Disulfonic Acid
50	12.8 --- ---	12.8	0.00	1063.63	Phenol Disulfonic Acid
51A	0.8 0.8 0.7	0.8	4.13	28.18	Phenol Disulfonic Acid
51B	1.5 1.1 1.0 1.0	1.2	12.50	13.64	Phenol Disulfonic Acid
51C	0.9 0.6 0.8	0.7	19.00	30.00	Phenol Disulfonic Acid
51D	1.4 1.4 1.4	1.4	0.00	27.27	Phenol Disulfonic Acid
51E	2.0 3.3 3.1	2.8	19.04	154.55	Phenol Disulfonic Acid
52	3.4 3.6 ---	3.5	2.86	218.18	Phenol Disulfonic Acid
53	--- --- ---	---	---	---	---
54	1.0 1.0 1.0	1.0	0.00	9.09	Brucine
55	3.7 3.1 3.7	3.5	7.63	218.18	Phenol Disulfonic "Model B"
56	2.0 3.0 2.0	2.3	18.83	111.82	Brucine

57	28 28 28	28	0.00	2445.45	Brucine "Model B"	
59	0.80 0.80 0.80	0.80	0.00	27.27	---	

Average of the means	1.98
Mean % deviation within labs	4.45
Mean % deviation from amount added	116.95
Median	1.0

SODIUM (19. 9 mg/l)
POTASSIUM (3. 1 mg/l)

The flame technique remains the most convenient method available for sodium and potassium measurements, and was employed by 35 laboratories for the sodium analysis and by 33 laboratories for the potassium. In both determinations the median figure reported was very nearly the true value, and the mean was 0. 9 mg/l high for sodium and 0. 1 mg/l high for postassium. There is undoubtedly a greater chance for sodium contamination of the sample by the operator, accounting for the greater deviations in the sodium data. The data indicates, however, that both sodium and potassium can be easily measured in normal waters, with or without special techniques, provided that extraneous sodium and potassium contamination are avoided.

SUMMARY OF Na, K ANALYSES

	Na	K
Amount added	19.9 mg/l	3.1 mg/l
Average deviation from amount added	±2.30 mg/l	±0.54 mg/l
Standard deviation from amount added	±2.62 mg/l	±0.52 mg/l
50% range	±1.1 mg/l	±0.30 mg/l
Method most commonly used	Flame	Flame
Total number of observations	42	36

LABORATORY COMMENTS
ON SODIUM METHOD

No. 7
Not done

No. 9
This is a very tedious method and time consuming.

No. 16
Routinely, this determination is only made by calculation after a complete chemical analysis.

No. 17
Not run

No. 18
This method is rather time consuming for our laboratory but it is the best available in the absence of a flame photometer. The evaporation of a 100 ml sample was accomplished in a 200 ml platinum dish by using a steam bath.

No. 21
Not run for lack of time. A flame photometer is not available in this laboratory.

No. 26
Not run

No. 27
Not run in this laboratory

No. 30
Not determined routinely

No. 32
Good duplication

No. 35
Sodium is run flamometrically. The difficulty with this procedure revolves around maintaining standards and keeping contamination out of the sample.

No. 36
Cleaning of gas jet with special cleaning tool helps get good ignition and better check results. Checking against standard before each unknown run is essential, as zero and maximum values tend to change slightly from run to run.

No. 37
This method of analysis has proven satisfactory for most waters.

No. 39
Not a routine test.

No. 42
We do not use internal standards. No difficulty encountered.

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Table 8. SODIUM (Amount added - 19.9 mg/l)

Lab. No.	Results	Mean	% dev. within labs.	% dev. from amt. added	Method
SEC	21.6 21.6 21.6	21.6	0.00	8.54	Flame
1	22.5 22.5 22.5	22.5	0.00	13.07	Flame
2	21 21 21	21	0.00	5.53	Flame
3	20 21 21	21	1.57	3.82	Flame
4	18 19 18	18	1.83	7.84	---
5	--- --- ---	---	---	---	---
6	19 19 19	19	0.00	4.52	Flame
7	--- --- ---	---	---	---	---
8	20 20 20	20	0.00	0.50	Flame
9	18 17 15	17	5.88	16.23	Gravimetric
10	21 24 23	23	4.35	13.92	Flame
11	19.3 19.8 19.8	19.6	1.19	1.31	Flame
12	20 20 20	20	0.00	0.50	Flame
13	--- --- ---	---	---	---	---
14	20 20 20	20	0.00	0.50	Flame
15	19.6 19.3 19.2	19.4	0.86	2.66	Flame
16	--- --- ---	---	---	---	---
17	--- --- ---	---	---	---	---
18	22 22 22	22	0.00	10.55	Gravimetric
19	11.4 11.8 11.9	11.7	1.71	41.21	Flame

20	20 20 21	20.3	2.10	2.16	Flame	30A	--- --- ---	---	---	---	---
21	20.4 20.8 20.5	20.6	0.81	3.32	Gravimetric	30B	--- --- ---	---	---	---	---
22	19 19 16	18	9.27	9.55	Flame	31	--- --- ---	---	---	---	---
23	--- --- ---	---	---	---	---	32	20.1 20.1 20.1	20.1	0.00	1.01	Flame with Photomultiplier
24	18 18 17	18	5.56	11.21	(Flame) Spectrophotometric	33	19.5 19.6 19.6	19.6	0.51	1.66	Flame
25	19.5 20.7 21.5	20.6	3.40	4.67	Flame	34	22.2 22.2 22.2	22.2	0.00	11.56	Flame
26A	--- --- ---	---	---	---	---	35A	21.7 --- ---	21.7	0.00	9.05	Flame
26B	--- --- ---	---	---	---	---	35B	21.7 --- ---	21.7	0.00	9.05	Calculation
27	--- --- ---	---	---	---	---	36	36.8 36.6 36.8	36.7	0.27	84.92	Colman Spec. and Flame
28A	--- --- ---	---	---	---	---	37	21 --- ---	21	0.00	5.53	Flame
28B	--- --- ---	---	---	---	---	38	18.9 19.1 19.0	19.0	0.35	4.52	Flame
29	--- --- ---	---	---	---	---	39	--- --- ---	---	---	---	---

40	--- --- ---	---	---	---	---
41	--- --- ---	---	---	---	---
42	21.0 21.0 21.0	21.0	0.00	5.53	Flame
43	--- --- ---	---	---	---	---
44A	35.0 --- ---	35.0	0.00	75.88	Flame
44B	--- --- ---	---	---	---	---
45	19.2 18.7 19.8	19.2	1.91	3.32	Uranyl-acetate
46	--- --- ---	---	---	---	---
47	20 20 20	20	0.00	0.50	Flame
48A	20 20 20	20	0.00	0.50	Flame
48B	--- --- ---	---	---	---	---
49	--- --- ---	---	---	---	---
50	--- --- ---	---	---	---	---
51A	20 20 20	20	0.00	0.50	Flame Beckman "DU"
51B	17 15 17 16	16.2	6.17	19.40	Flame
51C	20 20 21	20	1.65	2.16	Flame
51D	17 17 17	17	0.00	14.57	Flame
51E	21 19 20	20	3.35	3.52	Flame
52	--- --- ---	---	---	---	---
53	--- --- ---	---	---	---	---
54	20 21 22 22	21.0	4.76	9.05	Flame
55	18 18 18	18	0.00	9.55	Flame
56	20 21 20	20	1.65	2.16	Flame

57	---	---	---	---	---

	31.8				
59	28.3	30.1	3.88	51.09	---
	30.1				

Average of the means	20.8
Mean % deviation within labs	1.50
Mean % deviation from amount added	11.59
Median	20.0

LABORATORY COMMENTS ON POTASSIUM METHOD

No. 7
Not done

No. 9
This is a very long drawn out procedure and time consuming.

No. 16
Routinely, this determination is only made by calculation after a complete chemical analysis.

No. 17
Not run

No. 21
Not run for lack of time. A flame photometer is not available in this laboratory.

No. 24
Not done - Red Phototube not operating.

No. 26
Not run

No. 27
Not run in this laboratory

No. 30
Not determined routinely

No. 32
One sample was run using a radiation buffer of 500 ppm sodium in accordance with routine procedure. The result was 0.2 ppm lower than the results obtained using standards having 20 ppm sodium.

No. 35
Potassium is run flamometrically. There is not the difficulty in maintaining potassium standards or with contamination that characterizes the estimation of sodium.

No. 36
Check readings were a little more difficult to obtain than in the case of sodium.

No. 37
This method of analysis has proven satisfactory for most waters.

No. 39
Not a routine test

No. 42
Not a routine analysis

No. 45
Not done due to lack of time.

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Table 9. POTASSIUM (Amount added - 3.1 mg/l)

Lab. No.	Results	Mean	% dev. within labs.	% dev. from amt. added	Method
SEC	3.1 3.1 3.1	3.1	0.00	0.00	Flame
1	2.9 2.9 2.9	2.9	0.00	6.45	Flame
2	3.2 3.2 3.2	3.2	0.00	3.23	Flame
3	2.9 2.9 3.0	2.9	1.14	5.48	Flame
4	3.6 3.6 3.6	3.6	0.00	16.13	Flame
5	--- --- ---	---	---	---	---
6	3.3 3.3 3.3	3.3	0.00	6.45	Flame
7	--- --- ---	---	---	---	---
8	3.5 3.5 3.5	3.5	0.00	12.90	Flame
9	4.8 4.8 4.6	4.7	2.13	52.58	Sodium Cobal-Tinitrite
10	6.0 6.5 6.0	6.2	3.76	98.71	Flame
11	2.8 2.8 2.8	2.8	0.00	9.68	Flame
12	2.7 2.7 2.9	2.8	3.57	10.65	Flame
13	--- --- ---	---	---	---	---
14	3.5 3.5 3.5	3.5	0.00	12.90	Flame
15	2.8 2.8 2.7	2.8	1.18	10.65	Flame
16	--- --- ---	---	---	---	---
17	--- --- ---	---	---	---	---
18	--- --- ---	---	---	---	---
19	4.0 4.2 4.2	4.1	2.44	33.23	Flame

20	4.0 4.0 4.0	4.0	0.00	29.03	Flame	30A	--- --- ---	---	---	---	---
21	2.8 3.0 2.9	2.9	2.31	6.45	Silver Precip. & Titration - Imail & Harwood	30B	--- --- ---	---	---	---	---
22	3.1 3.1 3.0	3.1	1.06	0.97	Flame	31	--- --- ---	---	---	---	---
23	--- --- ---	---	---	---	---	32	3.2 3.2 3.0	3.1	3.23	3.23	Flame
24	--- --- ---	---	---	---	---	33	3.7 3.7 3.7	3.7	0.00	19.35	Flame
25	4.0 4.0 4.0	4.0	0.00	29.03	Flame	34	3.4 3.4 3.4	3.4	0.00	9.68	Flame
26A	--- --- ---	---	---	---	---	35A	3.1 --- ---	3.1	0.00	0.00	Flame
26B	--- --- ---	---	---	---	---	35B	--- --- ---	---	---	---	---
27	--- --- ---	---	---	---	---	36	3.2 3.2 3.2	3.2	0.00	3.23	Flame
28A	--- --- ---	---	---	---	---	37	3.6 --- ---	3.6	0.00	16.13	Flame
28B	--- --- ---	---	---	---	---	38	3.3 3.5 3.4	3.4	1.97	9.68	Flame
29	--- --- ---	---	---	---	---	39	--- --- ---	---	---	---	---

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40	---	---	---	---	---

41	---	---	---	---	---

42	---	---	---	---	---

43	---	---	---	---	---

44A	3.0	3.0	0.00	3.23	Flame

44B	---	---	---	---	---

45	---	---	---	---	---

46	---	---	---	---	---

	3.0				
47	2.9	3.0	1.10	4.19	Flame
	3.0				
	2.4				
48A	2.4	2.4	0.00	22.58	Flame
	2.4				

48B	---	---	---	---	---

49	---	---	---	---	---

50	---	---	---	---	---

	2.9				
51A	2.9	2.9	0.00	6.45	Flame
	2.9				
	2.3				
51B	2.7	2.6	5.77	23.23	Flame
	2.7				
	2.7				
51C	3.6	3.3	5.06	7.42	Flame
	3.1				
	3.3				
	1.9				
51D	1.9	1.9	0.00	38.71	Flame
	1.9				
	2.4				
51E	3.1	2.9	1.14	8.39	Flame
	3.2				

52	---	---	---	---	---

53	---	---	---	---	---

	3.0				
54	3.0	3.0	1.10	1.94	Flame
	3.1				
	0.4				
55	0.4	0.4	0.00	87.96	Flame
	0.4				

56	---	---	---	---	---

57	---	---	---	---	---

	3.3				
59	2.4	2.8	13.11	15.06	---
	2.6				

Average of the means	3.2
Mean % deviation within labs	1.39
Mean % deviation from amount added	17.36
Median	3.1

ALKALINITY (42.5 mg/l)

The procedures used for alkalinity measurement vary only in the choice of indicator or pH for determining the end point of the titration. The indicators include methyl orange, methyl purple, and mixed indicator. Only 6 of the 32 laboratories using an electrometric titration reported the pH chosen for the end point. These ranged from 4.3 to 4.7. The electrometric titrations had a standard deviation of 3.25 and the methyl orange figures had a standard deviation of 2.06. However, the methyl orange deviation is based on only 9 results. The commonly expressed failing of the methyl orange is the subjective error caused by inability of the individual analysts to detect subtle color changes. This, failing, apparently, may be minimized with experience. However, substitution of an objective physical end point for a subjective colored end point undoubtedly reduces the potential error.

SUMMARY OF ALKALINITY ANALYSES

Amount added	42.5 mg/l
Average deviation from amount added	± 3.14 mg/l
Standard deviation from amount added	± 3.50 mg/l
50% range	± 1.5 mg/l
Method most commonly used	Electrometric
Total number of observations	62

LABORATORY COMMENTS
ON ALKALINITY METHOD

No. 1
Using pink end point our alkalinity ran 175 ppm and up.

No. 7
End point better than with methyl orange method.

No. 10
Methyl orange used routinely on potable waters.

No. 13
Some people seem to have difficulty detecting the end point in this titration. However, most of our technicians are able to get good precision.

No. 18
The electrometric method employing the Beckman pH meter model H-2 is sufficiently accurate for our needs. The brom cresol green-methyl red indicator method requires experience to obtain a satisfactory end point at a pH of 4.8.

No. 30
For routine analysis we used an equivalence point of 4.8, using a pH meter. This seems quite satisfactory.

No. 37
In general, this method has proven to be satisfactory.

No. 42
End point much more distinct than methyl orange. Method simple and rapid.

No. 49
Difficult end point. Usually have to check pH to be sure.

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Table 10. ALKALINITY (Amount added - 42.5 mg/l)

Lab. No.	Results	Mean	% dev. within labs.	% dev. from amt. added	Method
SEC	42.2 41.8 42.2	42.1	0.40	1.01	pH Meter 4.5
1	39.0 39.0 39.0	39.0	0.00	8.24	Mixed Indicator
2	45 46 46	46	0.72	7.44	pH Meter 4.5
3	50 50 49	50	0.66	16.85	Automatic Titration
4	42 42 42	42	0.00	1.85	Electric Titrimeter
5	46 44 44	45	2.22	5.08	---
6	44 44 44	44	0.00	3.53	Methyl Purple
7	45.5 44.9 45.9	45.4	0.81	6.73	Mixed Indicator
8	43 44 43	43	0.77	1.95	Methyl Orange
9	44 42 44	43	2.33	2.73	---
10	--- --- ---	---	---	---	---
11	46 46 45	46	0.72	7.44	Methyl Purple
12	44 44 44	44	0.00	3.53	pH Meter
13	44 44 44	44	0.00	3.53	Methyl Orange
14	40 41 41	41	0.80	4.38	Mixed Indicator
15	40.7 41.2 41.2	41.0	0.57	3.44	Electro-metric
16	49.0 49.0 48.0	49.0	0.67	14.49	Mixed Indicator
17	50 50 50	50	0.00	17.65	Titration with HCl Methyl Purple Ind.
18	41 41 41	41	0.00	3.53	Electro-metric Mixed Indicator
19	46 46 46	46	0.00	8.24	pH Meter

20	43 42 41	42	1.60	1.95	pH Meter	30A	41.6 41.6 41.5	41.5	0.16	2.19	pH Meter
21	44.4 44.4 44.2	44.3	0.68	4.38	Titration Methyl Orange	30B	--- --- ---	---	---	---	---
22	43 43 44	43	0.77	1.95	Electro-metric Ti-tration 4.5	31	47 47 46	47	0.70	9.81	Electro-metric
23	38.9 38.9 38.9	38.9	0.00	8.47	Electro-metric (pH) Titration	32	42 40 41	41	1.63	3.50	Electro-metric
24	41 42 43	42	1.60	1.85	Mixed Acid Methyl Orange	33	40 40 40	40	0.00	5.88	Mixed Indicator pH 4.7
25	25.0 25.0 26.6	25.7	2.98	39.91	Titration	34	50.5 52.5 52.5	51.8	1.74	21.95	H_2SO_4 Titration
26A	39 39 38	39	0.85	9.01	Methyl Orange	35A	41 --- ---	41	0.00	3.53	Potentio-metric
26B	39 39 39	39	0.00	8.24	Electro-metric	35B	--- --- ---	---	---	---	---
27	48 48 48	48	0.00	12.94	pH Meter	36	40.0 42.5 42.5	41.6	2.72	1.95	Titration
28A		41	0.00	3.53	---	37	57 56 56	56	0.59	34.89	Potentio-metric
28B	--- ---	---	---	---	---	38	41.5 42.0 41.5	41.5	0.40	1.95	Electro-metric
29	43 42 42	42	0.79	1.18	---	39	47 44 44	45	2.96	5.88	Methyl Orange

40	44 44 44	44	0.00	3.53	---	50	40 46 ---	43	6.98	7.06	pH Meter Methyl Orange
41	44 45 44	44	0.75	4.31	---	51A	46 44 43	44	2.72	4.31	Potentio- metric
42	44 44 44	44	0.00	3.53	Methyl Purple	51B	45 42 42 43	43	2.33	4.71	pH Meter 4.5
43	40 41 ---	40.5	0.81	4.71	Methyl Purple	51C	48 47 46	47	1.43	10.59	Potentio- metric
44A	42 --- ---	42	0.00	1.18	Methyl Purple	51D	50 51 50	51	0.66	18.42	Potentio- metric
44B	--- --- ---	---	---	---	---	51E	44 48 46	46	2.89	8.24	pH Meter 4.5
45	40 42 45	42	3.98	4.31	Methyl Orange & pH Meter	52	--- --- ---	---	---	---	---
46	45 44 44	44	0.77	4.31	Methyl Purple	53	44 43 44	44	0.75	2.75	Methyl Orange
47	43 43 43	43	0.00	1.18	Potentio- metric	54	46 46 46	46	0.00	8.24	Electro- metric pH 4.3
48A	43 43 43	43	0.00	1.18	pH Meter	55	39 40 40	40	0.83	6.66	Beckman Autotrator
48B	--- --- ---	---	---	---	---	56	44 42 42	43	2.33	1.95	Methyl Orange
49	46 46 47	46	0.72	9.01	pH Meter Methyl Orange						
57	50 50 50	50	0.00	17.65	Methyl Orange						
59	52.6 52.6 55.0	53	1.76	25.65	---						

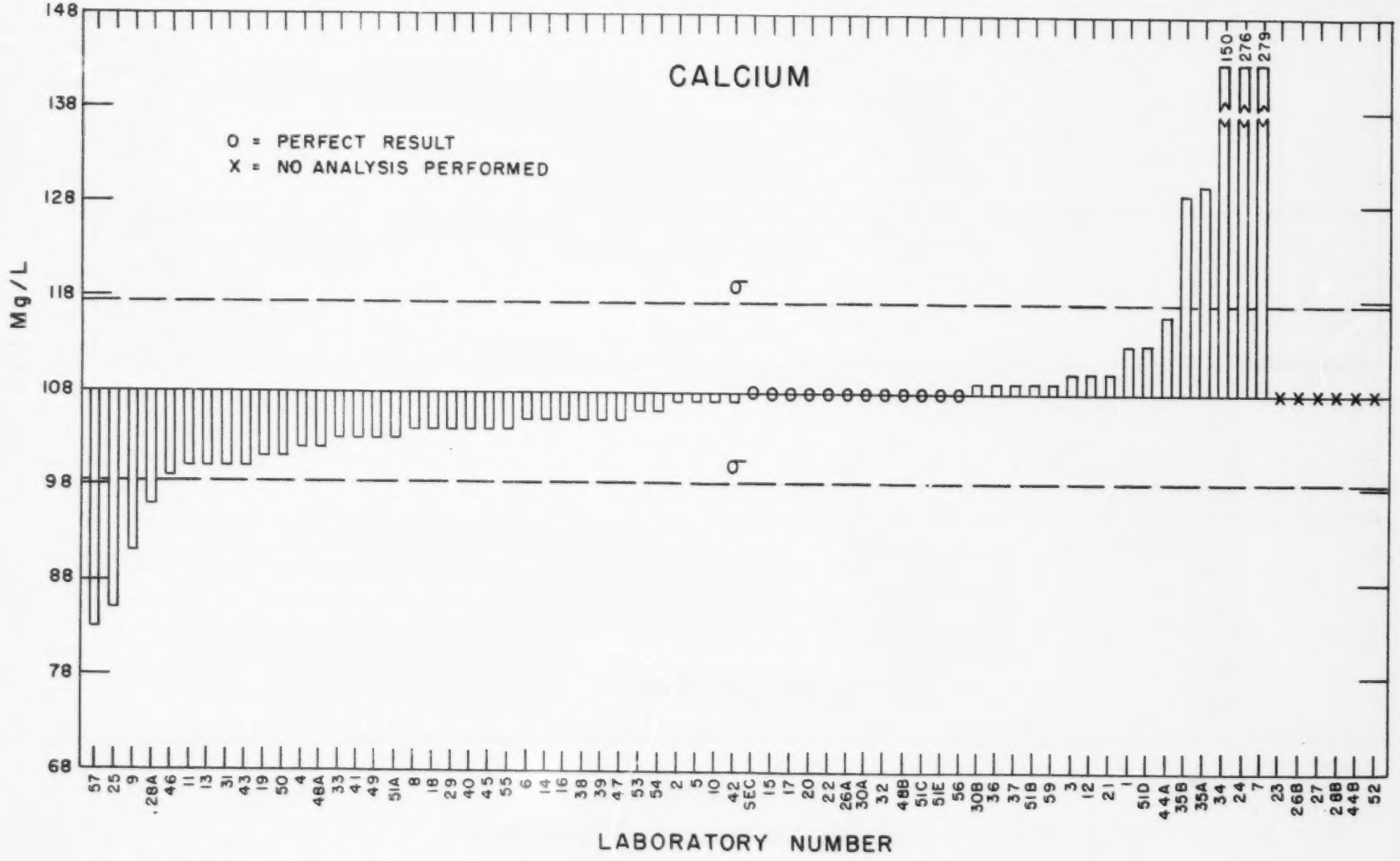
Average of the means	43.8
Mean % deviation within labs	0.98
Mean % deviation from amount added	7.42
Median	43.0

SUMMARY OF DATA

	Calcium	Magnesium	Chloride	Sulfate	Hardness	Nitrite	Nitrate	Sodium	Potassium	Alkalinity
Amount added, mg/l	108	82	241	259	610	0.25	1.1	19.9	3.1	42.5
Number of analyses	63	62	63	65	64	49	57	42	36	62
Arithmetic mean	112	90	237	249	605	0.28	1.98	20.8	3.2	43.8
Average deviation	10.9	13.8	10.5	21.9	18.0	0.09	1.29	2.30	0.54	3.14
Standard deviation	9.3	8.0	11.3	22.9	17.4	0.06	1.00	2.62	0.52	3.50
Number of methods used	4	3	6	5	4	1	6	4	3	4
Method #1	EDTA	Calculated	Mohr	Gravimetric	EDTA	Diazotization	Phenoldisulfonic	Flame	Flame	Electrometric
Number of users	45	39	41	32	56	49	40	35	33	32
Standard deviation	9.8	7.1	10.0	11.9	17.4	0.06	1.14	3.59	0.49	3.25
Method #2	Volumetric permanganate	Gravimetric	Mercuric nitrate	Turbidimetric	Insufficient data	---	Brucine	Gravimetric	Insufficient data	Methyl Orange
Number of users	5	9	9	19	---	---	8	3	---	9
Standard deviation	3.7	6.6	7.8	23.9	---	---	0.49	2.25	---	2.06

ANALYTICAL REFERENCE SERVICE

WATER-MINERALS No. 3



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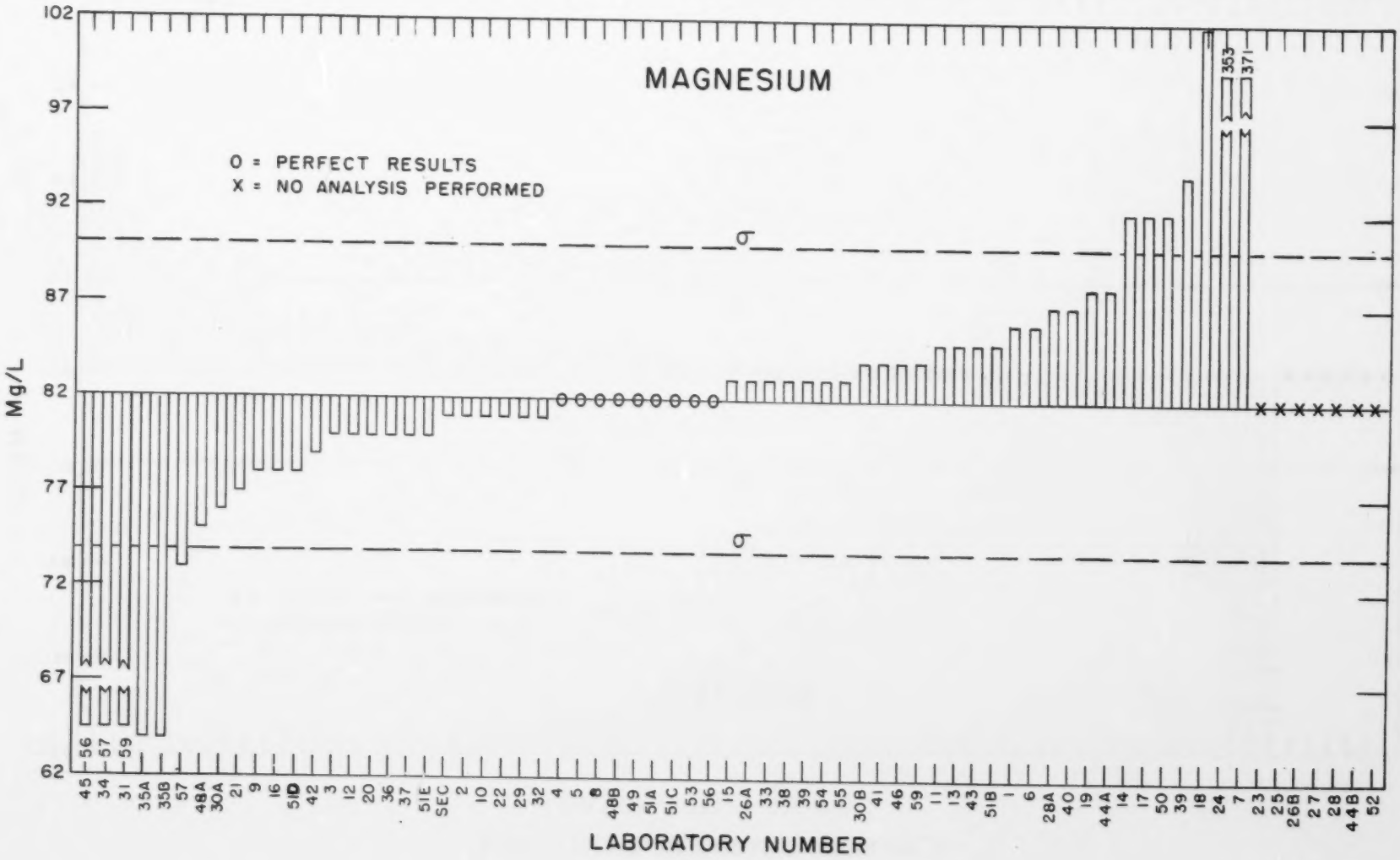

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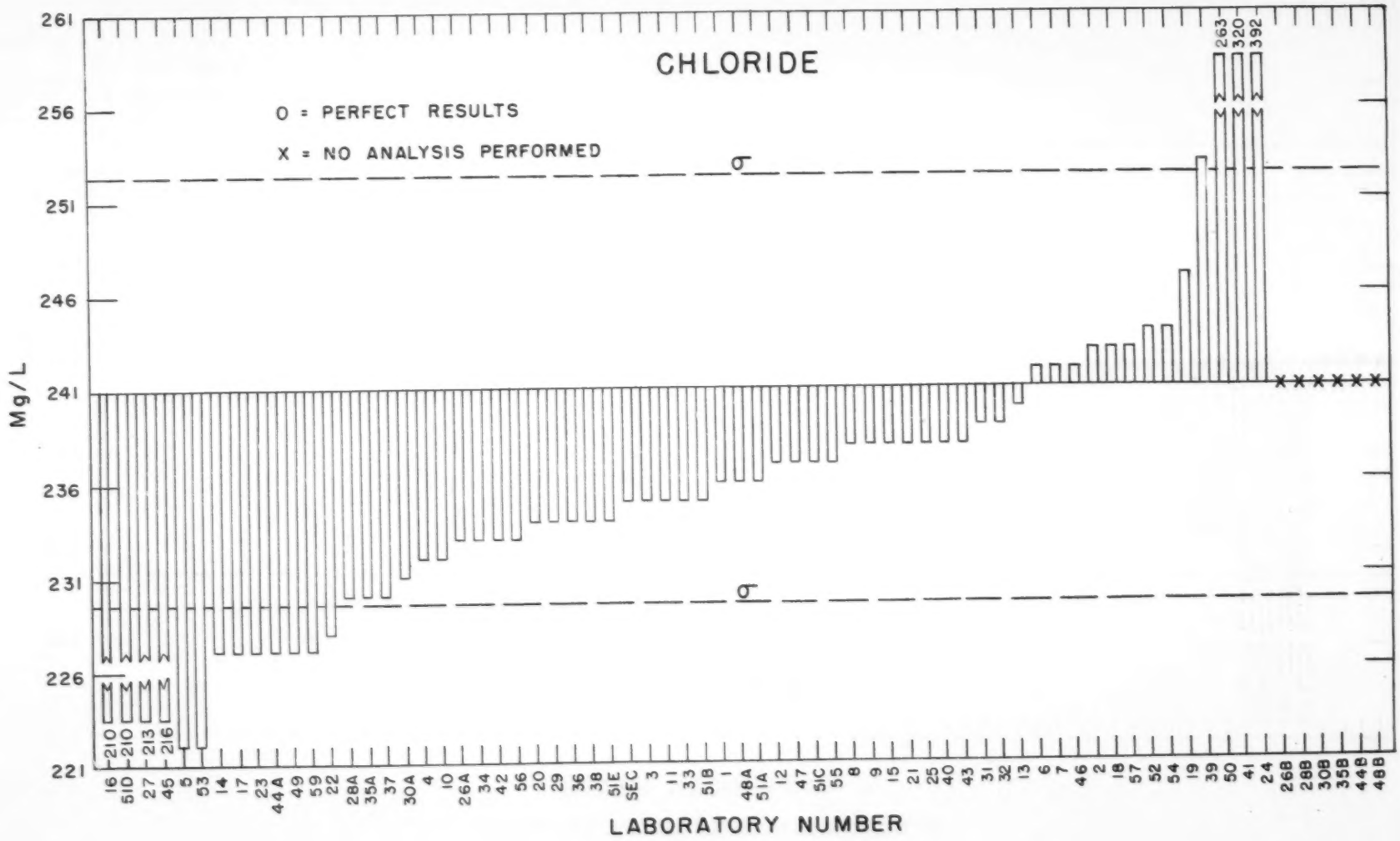

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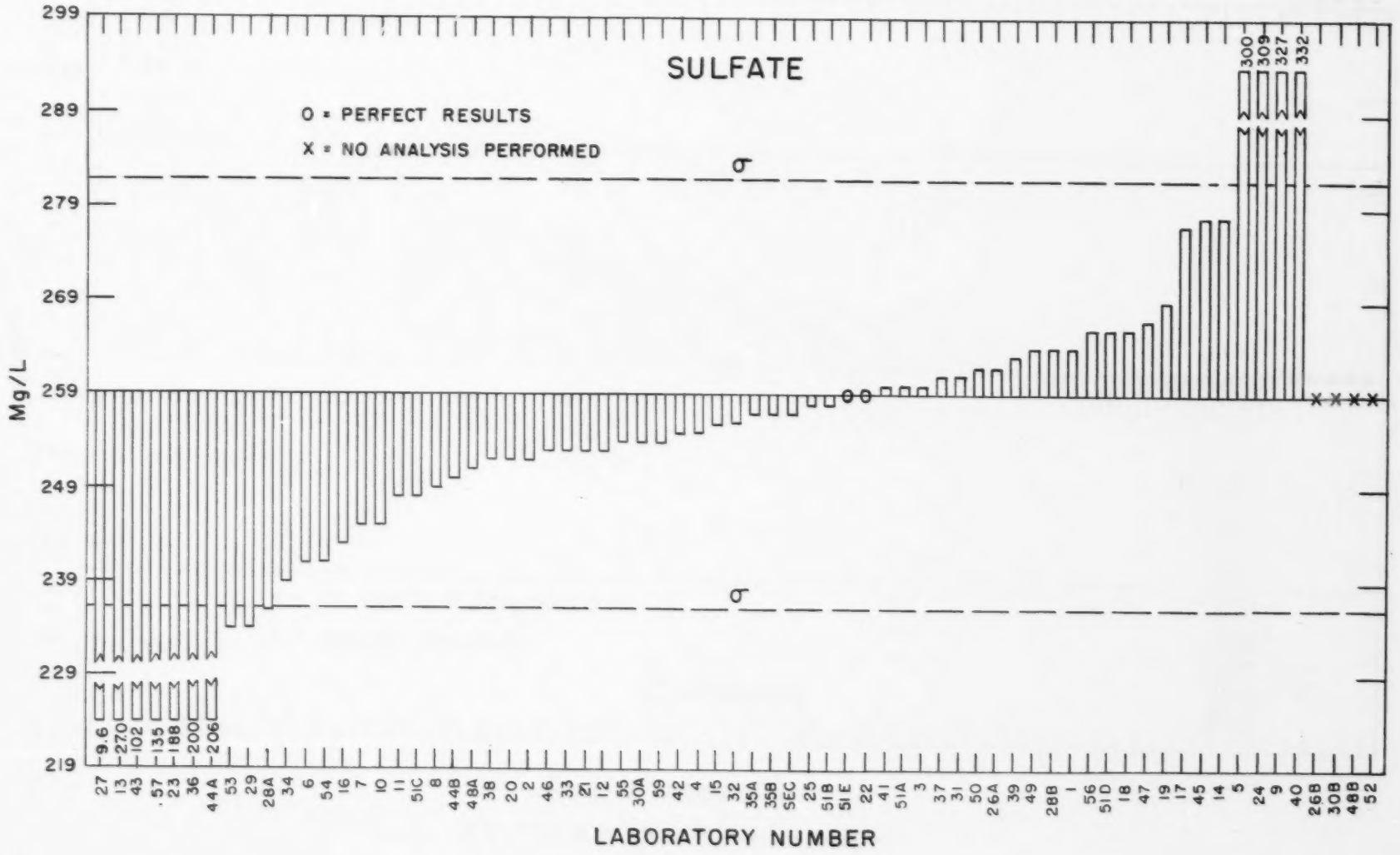

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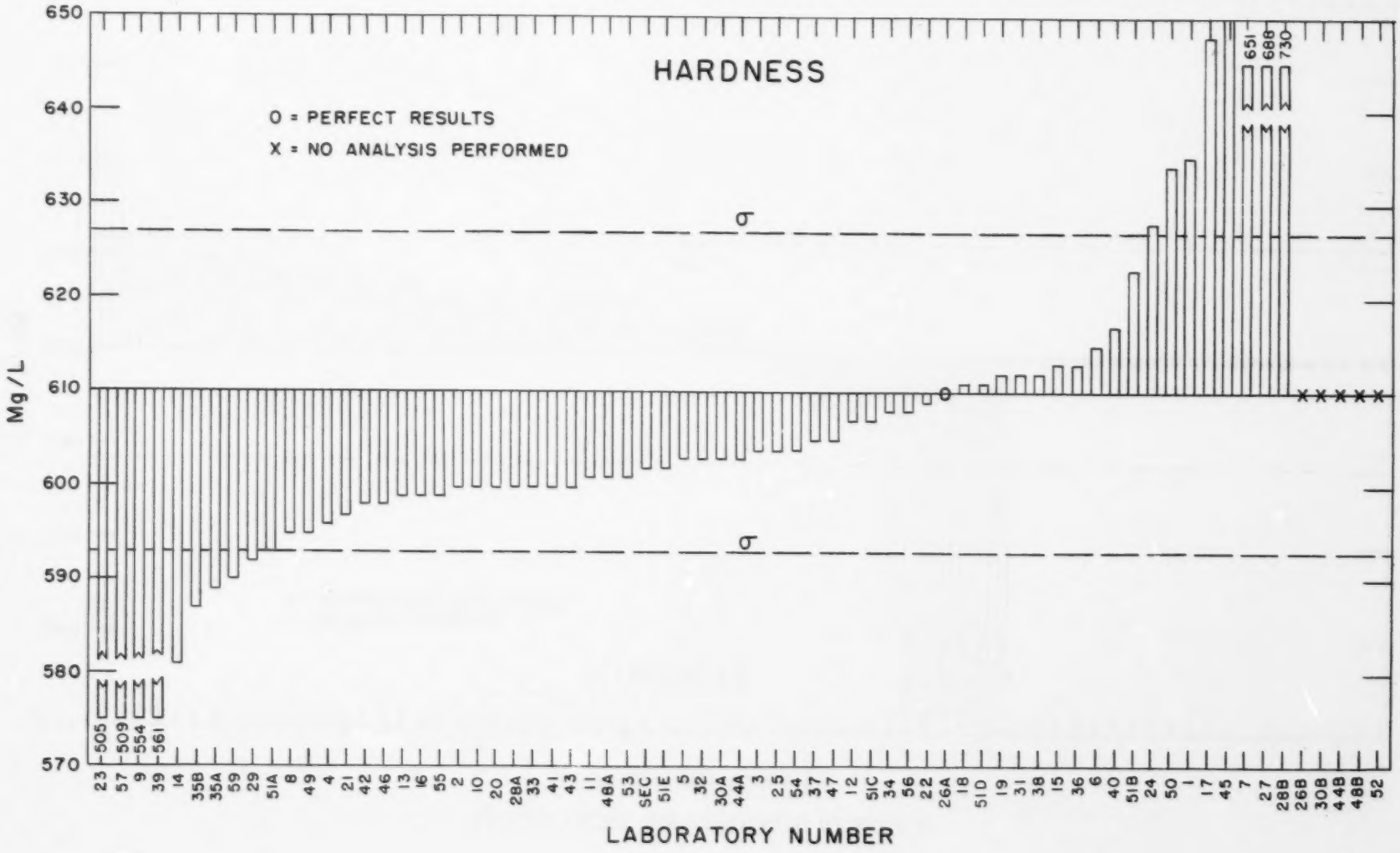

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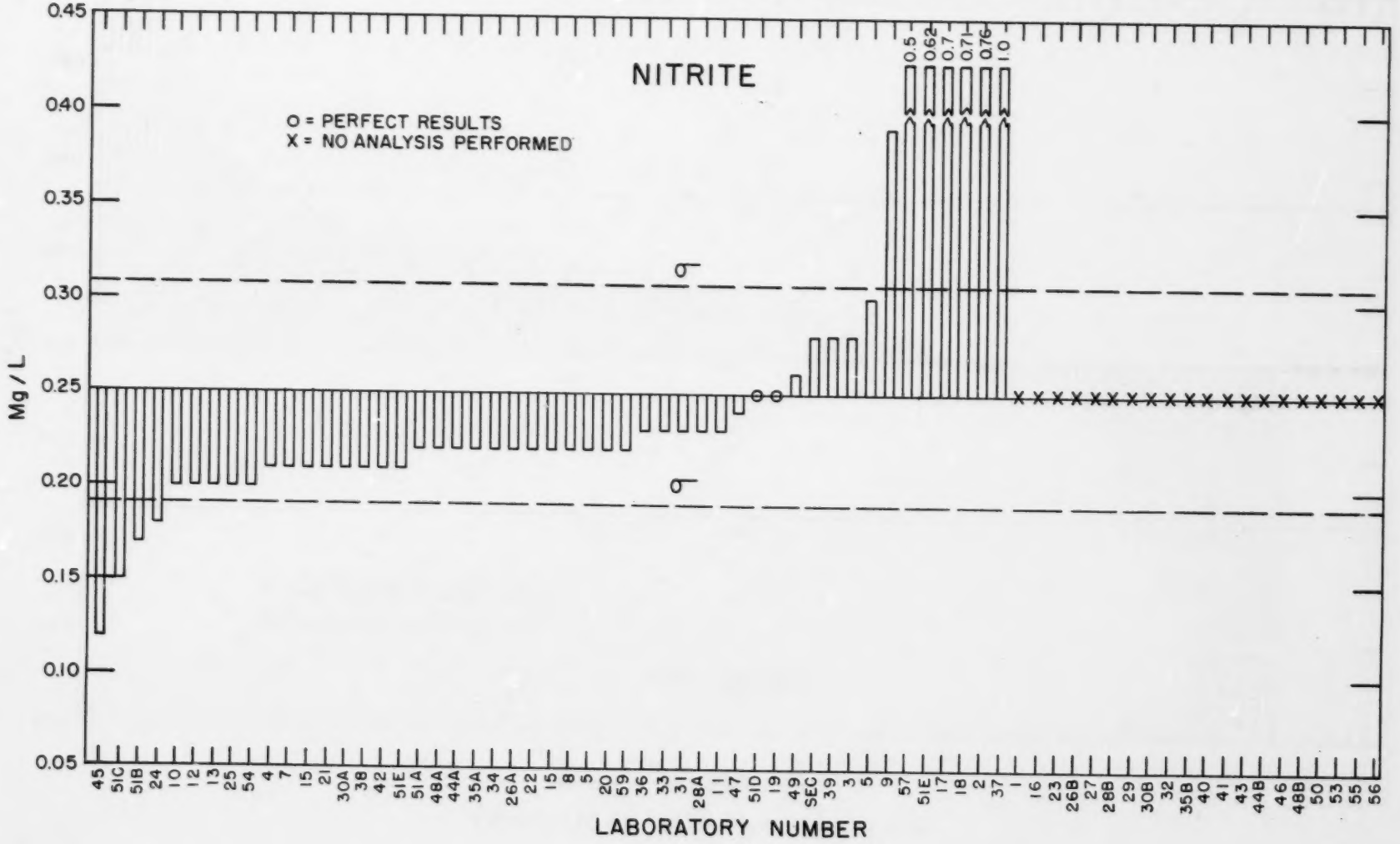

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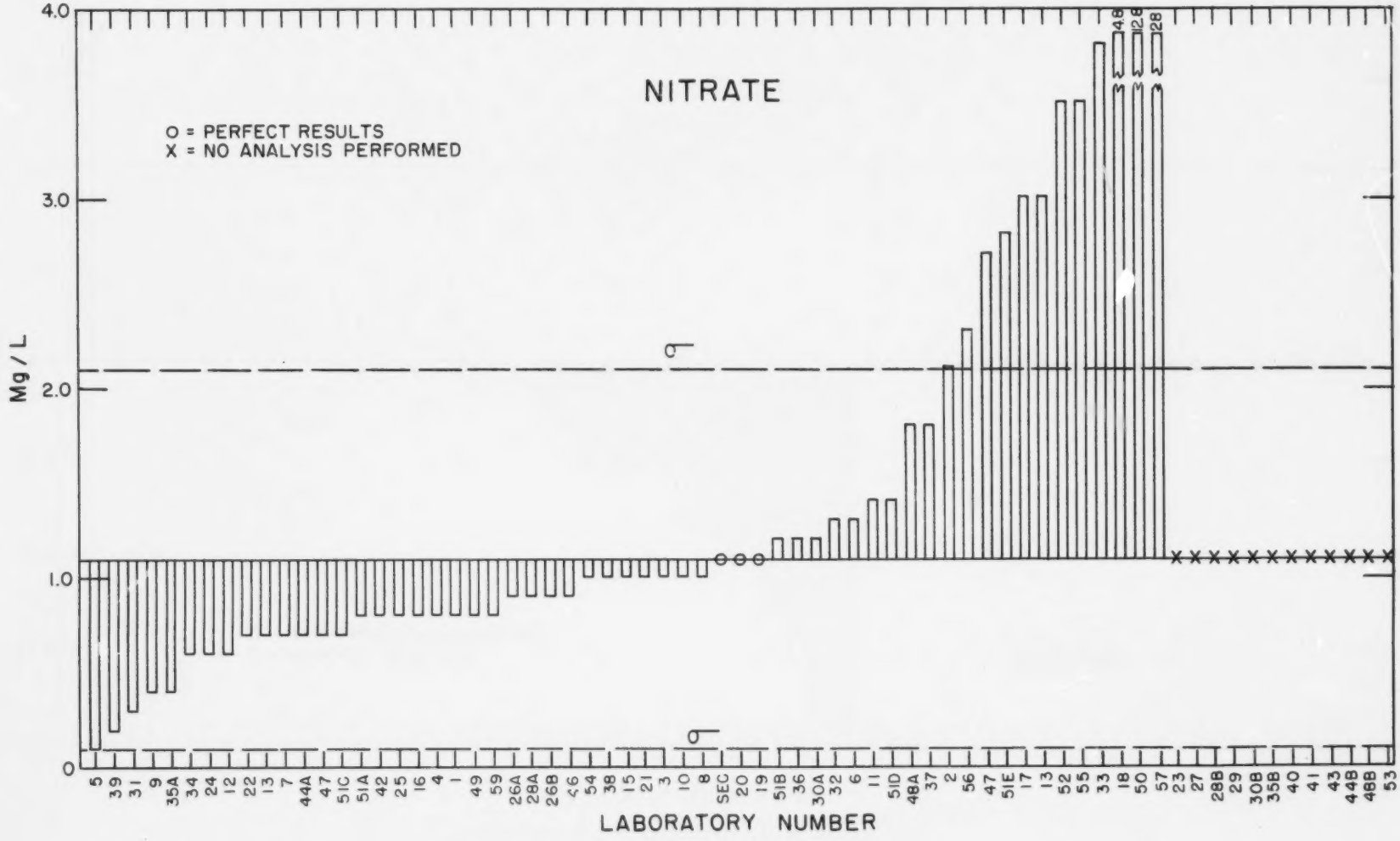

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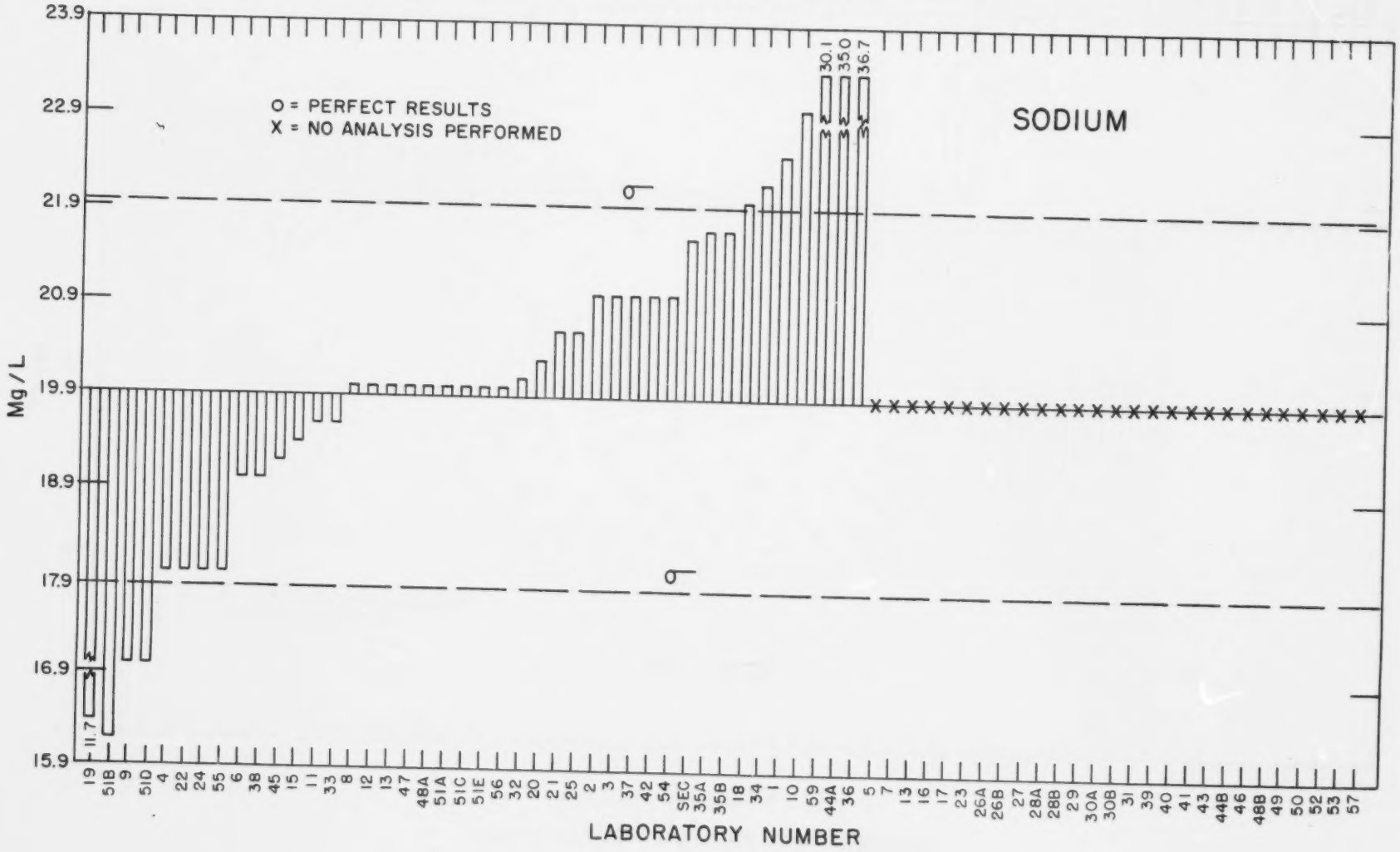

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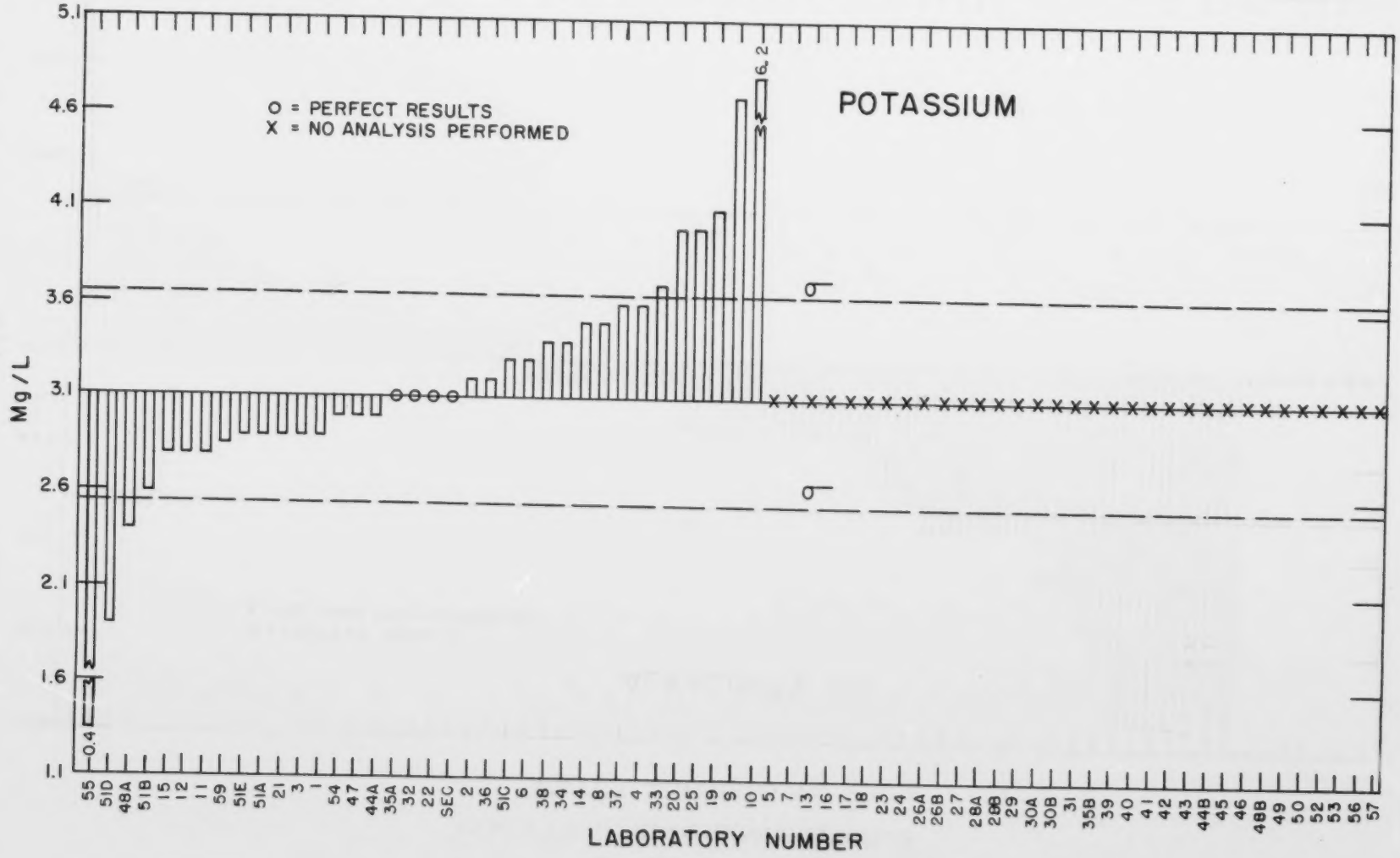

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